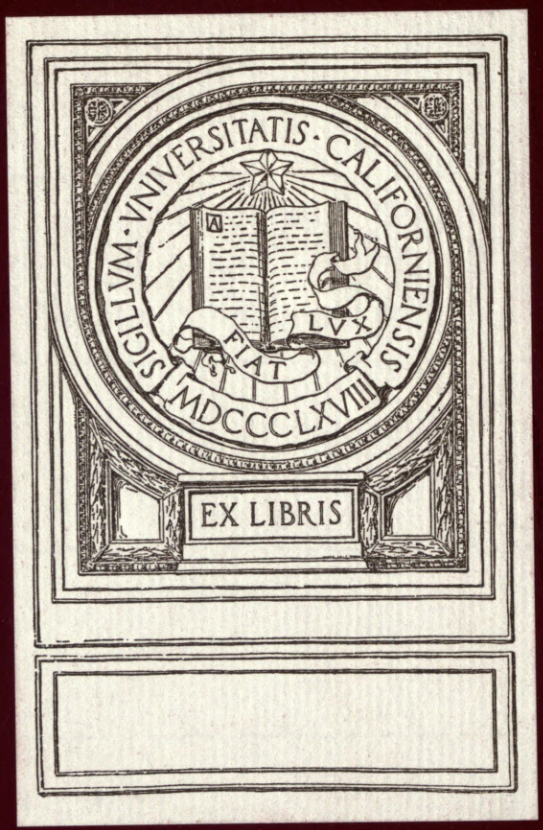
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SCIENTIFIC PAPERS

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UNIVERSITY OF SAINT ANDREWS

FIVE HUNDREDTH ANNIVERSARY

MEMORIAL VOLUME

OF

SCIENTIFIC PAPERS

Contributed by Members of the University

EDITED BY

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PUBLISHED BY THE UNIVERSITY

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PREFACE

THIS volume of papers is published with a twofold object: that the distinguished scientific guests of the University should receive an appropriate remembrance of their sojourn amongst us during the celebration of the five hundredth anniversary of Saint Andrews University was the first consideration; the second was that the present happy occasion affords a favourable opportunity for making a record, in some measure typical, of the kind and quality of the scientific research that is being pursued at this time by her children. The editors have been more concerned with the delineation of the picture, which they hope is presented within these covers, of the real unadorned intellectual work that is being performed by the members of the University than with the introduction of highly technical or elaborate studies. They are well aware that many of her distinguished graduates have given, and are giving, to the world scientific literature of the highest standard; and they are equally aware of the limitations imposed by time and space upon the selection that they have made for this volume. They feel that careful study of the authors' names will convince the candid reader that an attempt has been made to give a catholic representation of the present scientific life at Saint Andrews and at Dundee.

They have included work from professors, from assistants, and from graduates, some of whom have but recently emerged

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from tutelage ; they have also included papers from members of the University who are now working elsewhere.

On an occasion like the present even the strict and logical realm of Science cannot but be enveloped by the glamour inseparable from the circumstances which have called forth this book, and influenced by the thoughts that arise naturally from the consideration of the great space in time that lies between the rude beginnings of the University and the elaborate development of these later years.

Amidst the reflections evoked none is stronger, and none should be more reverently valued by the disciple of Science, than that which reminds us of the debt which we owe to those who have gone before us. To the deep and difficult foundations that they laid, to their patient and sometimes thankless and unrewarded labour, labour too often performed with scanty or ill-adapted tools, we owe our present points of vantage, our present ambitious intellectual structures. They have laboured, and we have indeed entered into their labours.

To their memory we dedicate this book, in the humble hope that in the future history of our dear University some memory may also remain of our familiar friends as helpers in carrying the torch of learning into still unillumined recesses ; in extending the empire of the human intellect ; and in giving to their fellowmen a nearer vision of the absolute yet ever unattainable truth.

J. E. A. STEGGALL

Chairman of the Editorial Committee

PRAEFATIO

Huius libri edendi illa ratio erat, primum ut viri doctissimi rerum naturae indagandae dediti munusculo quodam accepto meminissent se apud Andreanos, dum Almae Matris natalis quingentesimus celebraretur, per aliquos dies commorari; deinde quod hoc tam felici tempore oblata erat occasio exemplis quodam modo idoneis demonstrandi qua ratione, quanta diligentia nostrates rerum naturam exquirere conarentur.

Quem librum cum ei quibus hoc curae fuit componere vellent, illud magis sibi proponendum censebant, ut sine fuco et fallaciis docerent qualibus in studiis Andreani versarentur, quam ut opera exquisita arte elaborata in medium proferrent. Sciebant sane complures nostrorum libellos in quibus de rerum natura quaereretur et scripsisse optimos et scribere; praeterea se multa, dum hunc librum intra breve temporis spatium edere conantur, invitos omisisse. Illud vero persuasum sibi habebant, si quis scriptorum nomina diligenter perlegisset, eum affirmare non dubitaturum id saltem temptatum esse, ut demonstraretur quo modo cum Andreapoli tum Taoduni haec studia vigerent. Etenim alia professores scripserunt, alia lectores, alia alumni quorum nonnulli modo e statu pupillari excesserunt, alia qui antea apud nos versati, nunc alibi in his studiis versantur.

Atque hoc tali tempore eis quoque qui omnia diligenter perpendere et ad certam rationis normam dirigere solent

necesse est profecto ut mentis aciem praestringat illius diei species, dum secum reputant quanta interfuerit annorum series inter initia illa Academiae humillima atque hunc florentissimum eiusdem statum. Illud vero summa diligentia, summa reverentia recordari decet, illis qui ante nos operam in rerum natura indaganda collocaverunt maximam a nobis deberi gratiam. Nam quod illi semper summa patientia, interdum nulla gratia nullo munere, saepe vel paucis vel male aptis instrumentis quasi fundamenta iacere moliti sunt, idcirco nos iam haec excelsa aedificia tenemus, in hoc tam sublimi fastigio stamus. Illi laboraverunt, et nos in labores eorum introivimus.

Itaque illis hunc librum ita dicatum volumus ut simul sperare audeamus nonnullam apud posteros servatum iri memoriam amicorum quoque et familiarium nostrorum qui doctrinae facem in penetralia etiam nunc luce carentia inferre, ut latius mens humana dominetur efficere, denique ad scientiam illam perfectam atque absolutam, quam tamen nemo umquam assequi possit, propius accedere pro virili parte contendunt.

T. R. M.

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MATHEMATICS AND PHYSICS

CONCRETE REPRESENTATIONS OF NON-EUCLIDEAN GEOMETRY

Introductory Note

When Euclid composed his logical system of the Elements of Geometry he was no doubt aware that it was based upon many unproved assumptions. Some of these assumptions are explicitly stated, either as postulates or as axioms (or common notions). The fifth postulate, often given as the eleventh or the twelfth axiom, is a lengthy statement relating to parallel straight lines, and is conspicuous by its want of any intuitive character: 'If a straight line falling on two straight lines make the interior angles on the same side less than two right angles, the two straight lines, if produced indefinitely, meet on that side on which are the angles less than two right angles.' The universal converse of this statement is proved (with the help of another assumption, that the straight line is of unlimited extent) in Prop. 17, while its contrapositive is proved (again with the same assumption) in Prop. 28 of the First Book. Such considerations induced geometers and others to attempt its demonstration. Hundreds of such attempts have been made, with a display of great ingenuity. All these attempts, however, if they do not actually involve fallacious reasoning, are based upon some equivalent assumption either tacit or expressed.

An entirely different mode of attack was devised by a Jesuit, Gerolamo Saccheri.[1] He attempted to discover con-

[1] G. Saccheri, *Euclides ab omni naevo vindicatus*, Milan, 1733. This work was for a long time forgotten. It was brought to the notice of Beltrami in 1889, who published an account of it in the *Rendiconti* of the Lincei Academy. It has been translated into English by G. B. Halsted, *Amer. Math. Mon.*, 1-5 (1894-98), German by Stäckel and Engel in *Theorie der Parallellinien*, 1895, and Italian (*Manuali Hoepli*, 1904).

tradictions in the systems of geometry which would be evolved from a contrary assumption. The two geometrical systems which he develops at some length, which are characterised by the sum of the angles of a triangle being greater or less than two right angles, are the well-known non-Euclidean geometries, called by Klein Elliptic and Hyperbolic respectively. Saccheri himself, as also Lambert,[1] who struck out the same line independently, believed that the geometry of Euclid was the only logical system, and it was not till Lobachevsky [2] published the first of his epoch-making works in 1829 that non-Euclidean geometry emerged as a system ranking with Euclid's. With the name of Lobachevsky must always be associated that of Bolyai János, who arrived independently at the same results by similar methods. His work [3] was published as an appendix to a book of his father, Bolyai Farkas, in 1832. While Saccheri and Lambert both develop the two non-Euclidean geometries, neither Lobachevsky nor Bolyai admitted the possibility of Elliptic geometry, which requires that a straight line be of finite extent. To Riemann [4] is due the conception of finite space, but in his Spherical geometry two straight lines intersect twice like two great circles on a sphere. The conception of Elliptic geometry, in which the

[1] J. H. Lambert, 'Theorie der Parallellinien,' *Leipziger Mag. r. ang. Math.*, 1786. Reprinted in Stäckel and Engel's *Theorie der Parallellinien.*

[2] N. I. Lobachevsky, [On the Foundations of Geometry] (In Russian. German translation by Engel, Leipzig, 1898). *Geometrische Untersuchungen zur Theorie der Parallellinien*, Berlin, 1840 (2nd ed., 1887), has been translated into English by Halsted (Austin, Texas, 1891). One of the most accessible of his papers is 'Géométrie imaginaire,' *J. Math.*, Berlin, 17 (1837). Several other papers, originally composed in Russian, have been translated into French, German, or Italian. Lobachevsky's researches first became generally known by means of the translations of Hoüel in 1866-67.

[3] J. Bolyai, 'Appendix, Scientiam spatii absolute veram exhibens,' Maros-Vásárhely, 1832. Translated into English by Halsted (Austin, Texas, 1891).

[4] B. Riemann, 'Über die Hypothesen, welche der Geometrie zu Grunde liegen,' Göttingen, *Abh. Ges. Wiss.*, 13 (1866). The work was written in 1854, but was not published till after the death of the author. English translation by Clifford, *Nature*, 8 (1873).

straight line is finite, and is, without any exception, uniquely determined by two distinct points, is due to Klein.[1]

The method inaugurated by Saccheri has now been applied to most of the axioms or fundamental assumptions which lie at the basis of the Euclidean system, and a number of non-Euclidean geometries, many of them of considerable interest, have emerged. We shall be exclusively concerned, however, with the 'classical' non-Euclidean geometries, Hyperbolic (Lobachevsky-Bolyai) and Elliptic (Riemann-Klein).

While the development of Hyperbolic geometry in the hands of Lobachevsky and Bolyai led to no apparent internal contradiction, a doubt remained that contradictions might yet be discovered if the investigation were pushed far enough. This doubt was removed by the procedure of Beltrami,[2] who gave a concrete interpretation of non-Euclidean geometry by Euclidean geometry, whereby the straight lines of the former are represented by geodesics upon a surface of constant negative curvature (surface saddle-shaped at every point. The 'pseudosphere' or surface of revolution of the tractrix about its asymptote is a real surface of this description). Any contradiction in non-Euclidean geometry was thus shown to involve a contradiction in Euclidean geometry, and so both geometries must stand or fall together as *à priori* systems.

Several other concrete representations have been obtained, and it is proposed to discuss the most important of these.

§ 1. We shall confine ourselves almost entirely to the representations of plane non-Euclidean geometry, but the extensions to three dimensions will be indicated. We shall also consider for the most part only those representations in

[1] F. Klein, 'Über die sogenannte Nicht-Euklidische Geometrie,' *Math. Ann.*, 4 (1871), 6 (1873). French translation in *Ann. Fac. sc.*, Toulouse, 11G (1897).

[2] E. Beltrami, 'Saggio di interpretazione della geometria non-euclidea,' *Giorn. Mat.*, Napoli, 6 (1868). Extended to n dimensions in 'Teoria fondamentale degli spazii di curvatura costante,' *Ann. Mat.*, Milano (2), 2 (1868). Both translated into French by Hoüel, *Ann. Éc. Norm.*, Paris, 6 (1869).

which points are represented by points. To a point may correspond a single point or a system of points. In the latter case the system of points must be regarded as a single entity, and a curve which corresponds to a curve passing through a point P must pass through all the points which correspond to P. The representation is in fact effected by a point-transformation. The straight lines of the geometry will be represented by a system of curves depending upon two parameters; and in general any curve of the system must be uniquely determined when it has to pass through two distinct points. In addition to such considerations, which belong to *analysis situs*, it will be necessary also to establish the relations between the metrical properties of the geometry and those of its representation; we must determine the function of the positions of two points which corresponds to their *distance*, and the function of the positions (or parameters) of two curves representing straight lines which corresponds to the *angle* between them. The distance and angle functions are not independent, for a circle may be defined either as the locus of a point which is equidistant from a fixed point, or as the envelope of a line which makes a constant angle with a fixed line, or again as the orthogonal trajectory of a pencil of lines.

The Cayley-Klein Projective Metric

§ 2. The simplest representation which suggests itself is obtained by representing straight lines by straight lines. The projective properties of non-Euclidean geometry are identical with those of Euclidean geometry if we take into account imaginary and infinitely distant elements. Projective geometry is independent of the parallel-postulate. It is only in regard to metrical properties that there is any distinction between non-Euclidean geometry and its representation by the straight lines of ordinary geometry. Now Cayley [1]

[1] A. Cayley, 'A Sixth Memoir upon Quantics,' *Phil. Trans.*, 149 (1859), Math. Papers, vol. ii. Cayley wrote a number of papers dealing specially with non-Euclidean

showed—and his methods were elaborated by Klein [1]—that the metrical properties of figures are projective properties in relation to a certain fundamental figure, the *Absolute*, which in ordinary plane geometry is a degenerate conic consisting of the line infinity and the pair of imaginary points (circular points at infinity) through which all circles in the plane pass, but in non-Euclidean geometry is a proper conic, real in Hyperbolic, imaginary in Elliptic geometry. In the language of group-theory this is explained by saying that the group of motions, Euclidean or non-Euclidean, is a sub-group of the general projective group, and is characterised by leaving invariant a certain conic.[2]

§ 3. In ordinary plane geometry the metrical properties of figures are referred to a special line, the line infinity, u, and two special (imaginary) points on this line, the circular points at infinity, ω, ω'.

The line infinity appears in point-coordinates as an equation of the first degree, $u=0$, while every finite point satisfies the

geometry, but although he must be regarded as one of the epoch-makers, he never quite arrived at a just appreciation of the science. In his mind non-Euclidean geometry scarcely attained to an independent existence, but was always either the geometry upon a certain class of curved surfaces, like spherical geometry, or a mode of representation of certain projective relations in Euclidean geometry.

[1] *Loc. cit.*, p. 5, foot-note 1. Klein has written a great deal relating to non-Euclidean geometry, and was one of the first to apply it, especially in the conform representation, to the theory of functions. His Erlanger Programm, *Vergleichende Betrachtungen über neuere geometrische Forschungen*, 1872 (English translation in *Bull. Amer. Math. Soc.*, 2 (1893)), gives, in very condensed form, a number of representations of non-Euclidean geometry, especially in relation to Lie's theory of groups.

[2] The following elementary account of the Cayley-Klein representation was published in the *Proc. Edinburgh Math. Soc.*, 28 (1910). A simple exposition from the point of view of elementary geometry was given by Professor Charlotte A. Scott in the *Bull. Amer. Math. Soc.* (2), 3 (1897). An analytical treatment is also given in her treatise on *Modern Analytical Geometry* (London, Macmillan, 1894). The literature of this representation is very extensive, as the Projective Metric, or, what comes to nearly the same thing, the use of Weierstrass' coordinates (see p. 28, foot-note 1), whereby the equation of a straight line is of the first degree, forms one of the most useful means of studying non-Euclidean geometry.

identity $u \equiv \text{const.}$ In trilinear coordinates, for example, if a, b, c are the sides of the triangle of reference, Δ, $u \equiv ax+by+cz \equiv 2\Delta$.

The circular points appear in line-coordinates as an equation of the second degree, $\omega\omega'=0$, while every ordinary line satisfies the identity $\omega\omega' \equiv \text{const.}$ In trilinear coordinates

$$\omega\omega' \equiv \xi^2+\eta^2+\zeta^2-2\eta\zeta\cos A-2\zeta\xi\cos B-2\xi\eta\cos C$$
$$\equiv (\xi-\eta e^{iC}-\zeta e^{-iB})(\xi-\eta e^{-iC}-\zeta e^{iB}) \equiv 4\Delta^2.$$

In rectangular cartesian coordinates, made homogeneous by the introduction of a third variable z, the equation of the line infinity is $z=0$, while for finite points $z=1$. The line-coordinates of the line $lx+my+nz=0$ are l, m, n, and in general $l^2+m^2=\text{constant}$. When the equation is in the 'perpendicular' form, for example, the constant is unity. But for the line infinity $l=0$ and $m=0$ so that $l^2+m^2=0$, and this is true also for any line $y=\pm ix+b$, *i.e.* for any line passing through one or other of the points of intersection of the line $z=0$ with the locus $x^2+y^2=0$.

Now an equation of the second degree in point-coordinates or in line-coordinates represents a conic. But the equation $l^2+m^2=0$ represents a degenerate conic consisting of two (imaginary) pencils of lines, since l^2+m^2 decomposes into linear factors. Similarly $z=0$ as a point-equation, when written $z^2=0$, represents a degenerate conic consisting of two coincident straight lines. These conics are just one conic considered from the two different points of view of a locus and of an envelope, for the reciprocal of the equation $l^2+m^2=cn^2$ is $c(x^2+y^2)=z^2$. When $c=0$ the point-equation represents a circle of infinite radius $z^2=0$, and the line-equation $l^2+m^2=0$ represents the two pencils of lines passing through the two points through which all circles pass. This degenerate conic is called the *Absolute*.

If we now replace the degenerate conic by a proper conic, we get a more general form of geometry, which includes ordinary Euclidean geometry as a special case. It also includes as special cases the geometries of Lobachevsky and

Riemann, the former when the conic is real, the latter when it is imaginary. There are obviously other cases—for example, when the conic degenerates to two distinct lines—and there will be corresponding systems of geometry. Most of these geometries are very bizarre. In one, for example, the perimeter of a triangle is constant. The only ones which at all resemble the geometry of experience are the three just mentioned.

§ 4. We have now to obtain the expressions for the distance between two points and the angle between two straight lines. As the absolute in ordinary geometry is less degenerate as an envelope than as a locus (the equation in line-coordinates being of the second degree) it will be simpler to take first the angle between two lines.

The expression must be such as to admit of extension to the case of a proper conic. Now Laguerre [1] has shown that the angle between two straight lines can be expressed in terms of a cross-ratio. Consider two lines $y=x\tan\theta$, $y=x\tan\theta'$, passing through 0. We have also through 0 the two (isotropic) lines, $y=ix$, $y=-ix$, which pass through the circular points. The cross-ratio of the pencil formed by these four lines is

$$(uu',\ \omega\omega')=\frac{\tan\theta-i}{\tan\theta'-i}\div\frac{\tan\theta+i}{\tan\theta'+i}$$

$$=\frac{e^{i\theta}}{e^{i\theta'}}\div\frac{e^{-i\theta}}{e^{-i\theta'}}=e^{2i(\theta-\theta')}.$$

Hence $$\theta'-\theta=\tfrac{1}{2}i\log(uu',\ \omega\omega').$$

We can now extend this to the general case. Through the point of intersection L of two straight lines p, q there are two lines belonging to the absolute considered as an envelope, viz., the two tangents from L. Call these x, y. The angle (pq) is then defined to be

$$k\log(pq,\ xy)$$

where k is a constant depending upon the angular unit employed.

[1] E. Laguerre, 'Note sur la théorie des foyers,' *Nouv. Ann. Math.*, Paris, 12 (1853).

It is usual to take $k=\frac{1}{2}i$ so that the angle between two rays which form one straight line is $\frac{1}{2}i \log 1=\frac{1}{2}i \,.\, 2in\pi=m\pi$. This corresponds to the circular system of angular measurement, and we see that the angle between two rays is periodic, with period 2π. The angle between two lines with undefined sense has, however, the period π. If the two lines are conjugate with respect to the absolute, $(pq, xy)=-1$, and the angle is $\frac{1}{2}\pi$. The two lines are therefore at right angles.

An analogous definition is given for the distance between two points. On the line l joining two points P, Q there are two points belonging to the absolute considered as a locus, viz., the two points of intersection with l. Call these X, Y. The distance (PQ) is then defined to be

$$K \log (PQ, XY)$$

where K is a constant depending upon the linear unit employed.

§ 5. To test the consistency of these two formulæ for distance and angle it is sufficient to show that a circle, defined as the locus of a point equidistant from a fixed point, cuts its radii at right angles.

Let the equation of the absolute, referred to two tangents OA, OB and the chord of contact AB, be $xy=z^2$. In a line $y=mx$ through O take the point P (x, y, z). Let OP cut the conic in X, Y, and the chord of contact in M. Let X (or Y) and P divide OM in the ratios $1 : k$ and $1 : p$. The coordinates of the points are: $O(0, 0, 1)$, $M(1, m, 0)$, $X(1, m, k)$, $P(1, m, p)$. If (OP) is constant, P describes a circle, and we have the cross-ratio

$$(OP, XY)=\text{const.}=\mu=\frac{k_2-p}{k_1-p}, \text{ where } k_2=-k_1=\sqrt{m}.$$

Hence
$$p=\sqrt{m}\,\frac{1+\mu}{1-\mu}.$$

Also
$$px=z \text{ and } py=mz.$$

Eliminating m we find the equation of the locus of P,

$$xy=\left(\frac{1-\mu}{1+\mu}\right)^2 z^2=\lambda z^2,$$

which is a conic having double contact with the absolute at A and B.

The equation of the tangent at $P(x_1y_1z_1)$ is

$$xy_1+x_1y=2\lambda zz_1,$$

and that of OP is $$xy_1=x_1y.$$

The pole of the line OP with respect to the absolute is $(-x_1, y_1, 0)$, and this lies on the tangent. Hence OP and the tangent are conjugate with respect to the absolute and are therefore at right angles.

§ 6. When the absolute is imaginary X, Y are conjugate imaginary points, and $\log(PQ, XY)$ is a pure imaginary. In order that the distance may be real, K must then be a pure imaginary, and, as in the case of angles, we see that distance is a periodic function with period $2\pi Ki$. By taking $K=\frac{1}{2}i$ the period becomes π, and we make linear measurement correspond with angular. This case will be seen to correspond to *spherical* geometry, but the period (the radius of the sphere being unity) is not π but 2π. This is exactly analogous to the case of two rays, or lines with defined sense. On the sphere two antipodal points define the same pencil of great circles, but with opposite sense of rotation. If we leave the sense of rotation undefined, then they determine exactly the same pencil, and must be considered identical, or together as forming a single point; just as two rays, which make an angle π, together form a single line. On the sphere two lines (great circles) determine two antipodal points or pencils of opposite rotations; two points determine two rays of opposite directions. It is convenient thus to consider antipodal points as identical, or we may conceive a geometry in which this is actually the case. This is the geometry to which the name *elliptic* is generally confined, the term *spherical* being retained for the case in

which antipodal points are distinct.[1] In the Cayley-Klein representation spherical geometry is conveniently excluded, since two lines only intersect once.

§ 7. Consider next the case where the absolute is a real proper conic. This divides the plane into two distinct regions which we may call the interior and the exterior, and it is of no moment whether the conic be an ellipse, a parabola, or a hyperbola. It is convenient to picture it as an ellipse. If the points P, Q are in different regions, then (PQ, XY) is negative and $\log(PQ, XY)$ is a complex number of the form $a+(2n+1)i\pi$, or simply $a+i\pi$, to take its principal value. a is zero only when $(PQ, XY)=-1$. $K\log(PQ, XY)$ also will in general be complex whatever be the value of K. Of course it is possible to choose $K=a-i\pi$, which would make the distance real, but for points in the vicinity of Q the distance (PQ) would still be complex. On the other hand, if P, Q are in the same region, (PQ, XY) is either real, when X, Y are real, or purely imaginary, when X, Y are conjugate imaginary points. Then by taking K either real or a pure imaginary we can make the distance between two points in the same region real when measured along a certain class of lines, purely imaginary when measured along another class: these are the lines which do or do not cut the absolute. Hence we are led to consider certain points and lines as *ideal*.

Suppose we consider points within the absolute as *actual* points. The line joining two actual points always cuts the absolute, and we must take K real. Then all points outside the absolute are ideal points, for the distance between an exterior point and an interior point is complex (or purely imaginary in the case of harmonic conjugates). If Q lies on the absolute, while P does not, (PQ, XY) is either zero or infinite and $\log(PQ, XY)$ is infinite. Hence the absolute is the assemblage of points at infinity. Two lines cutting in an

[1] Some writers have distinguished these two geometries as single or polar elliptic and double or antipodal elliptic.

actual point O make a real angle if k is a pure imaginary, since the tangents from O are conjugate imaginaries.

This then completes the representation of Hyperbolic Geometry. Actual points are represented by the points within a real proper conic. The conic itself consists of all the points at infinity, while points outside it are ideal.

§ 8. If now we consider points outside the absolute as actual points, there are two cases according as K is taken to be real or imaginary. In the first case the distance between two points will be imaginary if the line joining them does not cut the absolute. Such a line must therefore be considered ideal, and we get in any pencil of lines with an actual point as vertex a class of ideal lines and a class of actual lines, and these are separated by the two tangents to the absolute. As these tangents are real, k must now be taken to be real, and we get a system of angular measurement of an entirely different nature from that with which we are familiar. The period of the angle is now $2i\pi k$ which is imaginary, and complete rotation about a point becomes impossible. If the line q is a tangent to the absolute $\log(pq, xy)$ is infinite. The angle between two lines thus tends to infinity as one line is rotated. Further, if the line PQ touches the absolute $\log(PQ, XY)=0$, *i.e.* $(PQ)=0$, or the distance between any two points on an absolute line is zero. This curious result can be found to hold even in ordinary geometry if we consider imaginary points. If the line PQ passes through one of the circular points, so that $y_1-y_2=i(x_1-x_2)$, then

$$PQ^2=(x_1-x_2)^2+(y_1-y_2)^2=0.$$

§ 9. We have now to examine if the logarithmic expression for the distance between two points holds in ordinary geometry. In this case the two absolute points X, Y on any line PQ coincide, and $(PQ, XY)=1$. The distance between any two points would thus be zero if K is finite. As the distance between any two points must, however, in general be finite, it follows that we must make K infinite.

Let $PY=PX+\epsilon$ where ϵ is small.

Then

$$(PQ, XY)=\frac{PX}{QX}\cdot\frac{QX+\epsilon}{PX+\epsilon}=\left(1+\frac{\epsilon}{QX}\right)\div\left(1+\frac{\epsilon}{PX}\right)=1+\epsilon\left(\frac{1}{QX}-\frac{1}{PX}\right)$$

and $$(PQ)=K\log(PQ, XY)=K\epsilon\left(\frac{1}{QX}-\frac{1}{PX}\right).$$

Let K approach infinity and ϵ approach zero in such a way that $K\epsilon$ approaches a finite limit λ.

Then $$(PQ)=\lambda\cdot\frac{PQ}{PX\,.\,QX}.$$

Now to fix λ we must choose some point E so that $(PE)=1$, the unit of length. Then $$1=\lambda\cdot\frac{PE}{PX\,.\,EX}$$

and $$(PQ)=\frac{PX\,.\,EX}{PE}\cdot\frac{PQ}{PX\,.\,QX}=\frac{XE}{PE}\div\frac{XQ}{PQ}=(XP, EQ).$$

If we take P as origin $=0$,

$$(0Q)=(X0, EQ)=(0\infty, Q1)=\frac{0Q}{01}\div\frac{\infty Q}{\infty 1},$$

which agrees with the ordinary expression since $\frac{\infty Q}{\infty 1}=1$.

It will be noticed that this case differs in one marked respect from the case of elliptic geometry. In that system there is a natural unit of length, which may be taken as the length of the complete straight line—the period, in fact, of linear measurement; just as in ordinary angular measurement there is a natural unit of angle, the complete revolution. In Euclidean geometry, however, the unit of length has to be chosen conventionally, the natural unit having become infinite. The same thing appears at first sight to occur in the hyperbolic case, since the period is there imaginary, but, K being imaginary, iK is real, and this forms a natural linear standard. (Cf. § 27 (3).)

§ 10. It still remains for us to consider the cases in which the absolute degenerates as an envelope to two coincident points and as a locus to two straight lines which may be real, coincident or imaginary. In these cases k is seen to be infinite,

and it appears as in the analogous case just considered that there is now no natural unit of angle available, as the period is infinite. A unit must be chosen conventionally.

The geometries in the case in which k is infinite or real present a somewhat bizarre appearance, and are generally on that account excluded from discussion, the objection being that complete rotation about a point is impossible, and the right angle has no real existence. Yet, if we go outside the bounds of plane geometry, such geometries will present themselves when we consider the metrical relations subsisting on certain planes, ideal or at infinity.

Let us consider the case of hyperbolic geometry of three dimensions. Here the absolute is a real, not ruled, quadric surface, say an ellipsoid, and actual points are within. Actual lines and planes are those which cut the absolute, and the geometry upon an actual plane is hyperbolic. But an ideal plane cuts the absolute in an imaginary conic, and the geometry upon such a plane is elliptic. A tangent plane to the absolute cuts the surface in two coincident points and a pair of imaginary lines. The geometry on such a plane is the reciprocal of Euclidean geometry, *i.e.* the measurement of distances is elliptic while angular measurement is parabolic. In this geometry the perimeter of a triangle is constant and equal to π, just as in Euclidean geometry the sum of the angles is constant and equal to π. Now if we make use of the theorem that the angle between two planes is equal to the distance between their poles with respect to the absolute, we see that the geometry of a bundle of planes passing through a point on the absolute is Euclidean. The sum of the three dihedral angles of three planes whose lines of intersection are parallel is therefore always equal to π, a result which was obtained by Lobachevsky and Bolyai.[1]

[1] A complete classification of all the geometries arising from the Cayley-Klein representation in space of n dimensions will be found in the author's paper, 'Classification of Geometries with Projective Metric,' *Proc. Edinburgh Math. Soc.*, 28 (1910).

§ 11. An apparent extension of the Cayley-Klein theory, elaborated by Fontené [1] for space of n dimensions, deserves mention.

The absolute conic in the Cayley-Klein theory is the double conic of a transformation by reciprocal polars. If we replace this transformation by the general dualistic linear transformation there arise two distinct conics having double contact, the pole conic or locus of points which lie upon their corresponding lines, and the polar conic or envelope of lines which pass through their corresponding points. Consider any line l and a point A upon it. To A there corresponds a line a which cuts l in a point A'. Thus a homography is established between pairs of conjugate points A, A' on the line l. The double points Ω_1, Ω_2 of this homography are the points in which l cuts the pole conic. The distance (PQ) between two points P, Q on l can then be defined as

$$K \log (\Omega_1 \Omega_2, PQ).$$

The distance between two conjugate points P, P' is constant for the line l, but it varies for different lines. It may be called the parameter of the line.

By allowing K to vary the parameter could of course be made the same for all lines ; but it is impossible to adjust the system so that it may represent a geometry with the necessary degrees of freedom. In fact, since a motion consists of a collineation which leaves the absolute invariant, and since the general collineation leaves just three points invariant, these points must be the points of contact of the two conics and the pole of their chord of contact. The general motion is therefore impossible, the only possible motion being a rotation about a definite point, the pole of the chord of contact.

E. Meyer [2] has considered a further generalisation of these ideas by taking two independent conics as the absolute

[1] G. Fontené, *'L'hyperespace à $(n-1)$ dimensions. Propriétés métriques de la corrélation générale.* Paris, Gauthier-Villars, 1892.

[2] 'Über die Kongruenzaxiome der Geometrie,' *Math. Ann.*, Leipzig, 64 (1907).

figures for angular and linear metric. He remarks that in ordinary Euclidean geometry the conics which play the rôle of absolute are also distinct, namely the one is a double line and the other is a point-pair. We have seen above, however, that these are just different aspects of the same degenerate conic. The double line is the locus, or assemblage of point-elements, the point-pair or pair of imaginary pencils is the envelope, or assemblage of line-elements.

Conform Representation by Circles

§ 12. We shall next consider a very useful representation which has important applications in the theory of functions, that in which straight lines are represented by circles.[1] Since a circle requires three conditions to determine it, one condition must be given. Hence if the circle

$$x^2+y^2+2gx+2fy+c=0$$

represents a straight line, the constants, g, f, c, must be connected by a linear relation, which may be written

$$2gg'+2ff'=c+c'.$$

But this relation expresses that the circle cuts orthogonally the fixed circle

$$x^2+y^2+2g'x+2f'y+c'=0.$$

Hence *the circles which represent the straight lines of a geometry form a linear system cutting a fixed circle orthogonally.*

Similarly in three dimensions if planes are represented by spheres they will cut a fixed sphere orthogonally.

§ 13. Thus we find at once that there are three forms of geometry, according as the fundamental circle is real, vanishing, or imaginary.

A difficulty, however, presents itself. Two orthogonal

[1] An interesting account of this representation, from the point of view of elementary geometry, is given by H. S. Carslaw, *Proc. Edinburgh Math. Soc.*, 28 (1910). The following account, which was suggested by Professor Carslaw's paper, appeared in the same volume.

circles in general intersect in two points, which may be real, coincident, or imaginary ; and the point-pair thus determined will not determine uniquely one orthogonal circle, but a pencil of circles. Two such points are inverse points with respect to the fixed circle. We shall see in § 18 that the 'distance' between a pair of inverse points is real or imaginary according as the fundamental circle is imaginary or real. In the former case we may either consider the two points as distinct (so that two straight lines will intersect in two points), or identify them ; and we get the two forms of geometry, Spherical and Elliptic. In the latter case it is necessary to identify the two points, otherwise we should have two real points with an imaginary distance ; thus we get Hyperbolic geometry. Alternatively we may agree to consider only the points in the interior (or exterior) of the fundamental circle. When the fundamental circle reduces to a point O, one of the points of any point-pair is at O and we need only consider the other point, so that two lines always intersect in just one point. This geometry is Parabolic, and we shall see that it is identical with Euclidean geometry.

When the fundamental circle is real, two orthogonal circles intersect in two points, real, coincident, or imaginary. This corresponds to the three sorts of line-pairs in Hyperbolic geometry, intersectors, parallels, and non-intersectors. When the fundamental circle is imaginary, two orthogonal circles always intersect in two real points, so that in Elliptic or Spherical geometry parallels and non-intersectors do not exist. When the fundamental circle reduces to a point O, every orthogonal circle passes through O, and they cut in pairs in one other real point which may coincide with O. The latter case corresponds to parallels in Euclidean geometry.

§ 14. Next, to fix the representation, we have to consider the measurement of distances and angles.

Let us make the condition that angles are to be the same in the geometry and in its representation, *i.e.* that the repre-

sentation is to be conform.[1] We shall find that this fixes also the distance function.

First let us find how a circle is represented. A circle is the locus of points equidistant from a fixed point, or it is the orthogonal trajectory of a system of concurrent straight lines. Now a system of concurrent straight lines will be represented by a linear one-parameter system of circles, *i.e.* a system of coaxal circles. The orthogonal system is also a system of coaxal circles, and the fixed circle belongs to this system. Hence *a circle is represented always by a circle, and its centre is the pair of limiting (or common) points of the coaxal system determined by the circle and the fixed circle.*

The distance function has thus to satisfy the condition that the points upon the circle which represents a circle are to be at a constant distance from the point which represents its centre. To determine this function let us consider motions. A motion is a point-transformation in which circles remain circles ; and further, the fundamental circle must be transformed into itself, and angles must be unchanged.

§ 15. The equation of any circle may be written [2]

$$z\bar{z}+\bar{p}z+p\bar{z}+c=0$$

where $z=x+iy$, $p=g+if$ and $\bar{z}$, $\bar{p}$ are the conjugate complex numbers. Now the most general transformation which pre-

[1] C. E. Stromquist, in a paper 'On the Geometries in which Circles are the Shortest Lines,' New York, *Trans. Amer. Math. Soc.*, 7 (1906), 175-183, has shown that 'the necessary and sufficient condition that a geometry be such that extremals are perpendicular to their transversals is that the geometry be obtained by a conformal transformation of some surface upon the plane.' The language and his methods are those of the calculus of variations. The *extremals* are the curves along which the integral which represents the distance function is a minimum, *i.e.* the curves which represent shortest lines; and the *transversals* are the curves which intercept between them arcs along which the integral under consideration has a constant value. Thus in ordinary geometry, where the extremals are straight lines, the transversals to a one-parameter system of extremals are the involutes of the curve which is the envelope of the system. In particular, when the straight lines pass through a fixed point the transversals are concentric circles.

[2] Cf. Liebmann, *Nichteuklidische Geometrie* (Leipzig, 1905), §§ 8, 11.

serves angles and leaves the form of this equation unaltered is [1]

$$z=\frac{az'+\beta}{\gamma z'+\delta},\quad \bar{z}=\frac{\bar{a}\bar{z}'+\bar{\beta}}{\bar{\gamma}\bar{z}'+\bar{\delta}}.$$

This is a conformal transformation since any transformation between two complex variables has this property.

To find the relations between the coefficients in order that the fundamental circle may be unchanged, let its equation be

$$x^2+y^2+k=0 \text{ or } z\bar{z}+k=0.$$

This becomes $(az+\beta)(\bar{a}\bar{z}+\bar{\beta})+k(\gamma z+\delta)(\bar{\gamma}\bar{z}+\bar{\delta})=0.$

Hence $$a\bar{\beta}+k\gamma\bar{\delta}=0$$

and $$k(a\bar{a}+k\gamma\bar{\gamma})=\beta\bar{\beta}+k\delta\bar{\delta}$$

$$=k\delta\bar{\delta}+k^2\frac{\gamma\bar{\gamma}\,.\,\delta\bar{\delta}}{a\bar{a}},$$

therefore $$a\bar{a}=\delta\bar{\delta},$$

so that $$\frac{a}{\bar{\delta}}=\frac{\delta}{\bar{a}}=-\frac{k\gamma}{\bar{\beta}}=-\frac{\beta}{k\bar{\gamma}}=\lambda.$$

We have $a=\lambda\bar{\delta}$ and $\bar{a}=\bar{\lambda}\delta$, and also $\bar{a}=\frac{1}{\lambda}\delta$,

therefore $$|\lambda|=1.$$

The general transformation is therefore [2]

$$z'=\lambda\frac{az-k\beta}{\bar{\beta}z+a}, \text{ where } |\lambda|=1.$$

By any such homographic transformation the cross-ratio of four numbers remains unchanged, *i.e.*

$$(z_1z_2,\ z_3z_4)=(z'_1z'_2,\ z'_3z'_4).$$

[1] The only other type of transformation possible is

$$z=\frac{a\bar{z}'+\beta}{\gamma\bar{z}'+\delta},\ \bar{z}=\frac{\bar{a}z'+\bar{\beta}}{\bar{\gamma}z'+\bar{\delta}},$$

but this only differs from the former by a reflexion in the axis of x, $\bar{z}=z''$, $z=\bar{z}''$.

[2] When, as is often taken to be the case, the fundamental circle is the x-axis, the conditions are simply that the coefficients α, β, γ, δ be all real numbers.

To find the condition that this cross-ratio may be real, let θ_{ij} be the amplitude, and r_{ij} the modulus of $z_i - z_j$, then

$$(z_1z_2,\ z_3z_4)=\frac{r_{13}}{r_{14}}\frac{r_{24}}{r_{23}}e^{i(\theta_{13}-\theta_{14}+\theta_{24}-\theta_{23})}.$$

Hence we must have

$$\theta_{13}-\theta_{14}+\theta_{24}-\theta_{23}=m\pi,$$

and the four points z_1, z_2, z_3, z_4 are concyclic.

§ 16. Now to find the function of two points which is invariant during a motion; the two points determine uniquely an orthogonal circle, and if the transformation leaves this circle unaltered it leaves unaltered the two points where it cuts the fixed circle. Hence if these points are x, y, the cross-ratio $(z_1z_2,\ xy)$ for all points on this circle depends only on z_1 and z_2. If the distance function is $(PQ)=f\{(z_1z_2,\ xy)\}$ or, as we may write it, $f(z_1,\ z_2)$, then for three points P, Q, R, $(PQ)+(QR)=(PR)$, or

$$f(z_1,\ z_2)+f(z_2,\ z_3)=f(z_1,\ z_3).$$

This is a functional equation by which the form of the function is determined. Differentiating with respect to z_1, which may for the moment be regarded simply as a parameter, we have

$$f'(z_1,\ z_2)\cdot\frac{QY}{QX}\cdot\frac{d}{dz_1}\left(\frac{PX}{PY}\right)=f'(z_1,\ z_3)\cdot\frac{RY}{RX}\cdot\frac{d}{dz_1}\left(\frac{PX}{PY}\right).$$

Hence

$$\frac{f'(z_1,\ z_2)}{f'(z_1,\ z_3)}=\frac{QX}{QY}\frac{RY}{RX}=\left(\frac{PX}{PY}\frac{RY}{RX}\right)\div\left(\frac{PX}{PY}\frac{QY}{QX}\right)=\frac{(z_1z_3,\ xy)}{(z_1z_2,\ xy)},$$

and $$(z_1z_2,\ xy)f'\{(z_1z_2,\ xy)\}=\text{const.}=\mu.$$

Integrating, we have

$$f(z_1,z_2)=\mu\log(z_1z_2,\ xy)+C.$$

The constant of integration, C, is determined $=0$ by substituting in the original equation. Hence

$$(PQ)=\mu\log(z_1z_2,\ xy)=\mu\log\left(\frac{PX}{PY}\frac{QY}{QX}\right)=\mu\log(PQ,\ XY),$$

$(PQ,\ XY)$ being the cross-ratio of the four points P, Q, X, Y

on the circle, *i.e.* the cross-ratio of the pencil $O(PQ, XY)$ where O is any point on the circle.

§ 17. The expression for the line-element can now be found by making PQ infinitesimal.

We have, by Ptolemy's Theorem,

$$PX \,.\, QY = PQ \,.\, XY + PY \,.\, QX.$$

Hence $$ds = \mu \log\left(1 + \frac{PQ \,.\, XY}{PY \,.\, QX}\right) = \mu \frac{XY}{PX \,.\, PY} \,.\, PQ.$$

Let OP (Fig. 1) cut the circle PXY again in R and the fixed circle in A, B. Then R is a fixed point so that PR is constant.

Also $$\frac{RX}{PX} = \frac{RY}{PY} = \text{a fixed ratio} = e,$$

and $$PR \,.\, XY = PX \,.\, RY + PY \,.\, RX = 2e \,.\, PX \,.\, PY.$$

Therefore $\dfrac{XY}{PX \,.\, PY} = \dfrac{2e}{PR}$ and is therefore a function of the position of P alone.

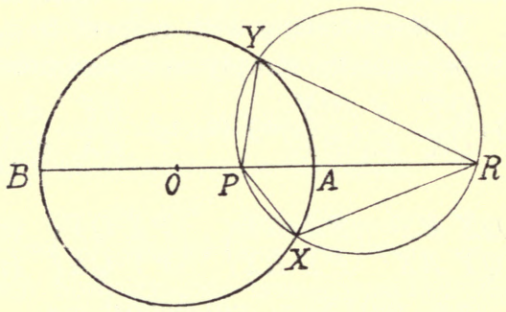

FIG. 1

To find its value we may take any orthogonal circle through P, say the straight line PR.

Then $$\frac{XY}{PX \,.\, PY} = \frac{AB}{PA \,.\, PB} = \frac{2\sqrt{-k}}{k + x^2 + y^2}.$$

Hence $$ds = \frac{2\mu\sqrt{-k}}{x^2 + y^2 + k} \sqrt{dx^2 + dy^2}.$$

§ 18. The distance function is thus periodic with period $2i\mu\pi$. If P, P' are inverse with respect to the fixed circle

$$(PP')=\mu\log\left(\frac{PA}{PB}\frac{P'B}{P'A}\right)=\mu\log(-1)=i\mu\pi,$$

and
$$(PQ')=\mu\log\left(\frac{PX}{PY}\frac{Q'Y}{Q'X}\right)=\mu\log\left(-\frac{PX}{PY}\frac{QY}{QX}\right)$$
$$=(PQ)+i\mu\pi.$$

When Q is on the fixed circle $(PQ)=\infty$. The fundamental circle is thus the assemblage of points at infinity.

If the fundamental circle is imaginary, k is positive and μ is purely imaginary and may be put $=i$. Then if inverse points are considered distinct their distance is π and the period is 2π, but if inverse points are identified the period must be taken as π.

If the fundamental circle is real, k is negative and μ is real and may be put $=1$. Then the period must be taken as $i\pi$ and inverse points must be identified, otherwise we should have two real points with an imaginary distance. In this geometry there are three sorts of point-pairs, real, coincident, and imaginary, or actual, infinite, and ultra-infinite or ideal.

§ 19. Now if we change x, y into x', y' with the help of an additional variable z' by the equations

$$\frac{x'}{x}=\frac{y'}{y}=\frac{z'-R}{\sqrt{k}}=\frac{2R\sqrt{k}}{x^2+y^2+k},$$

then
$$x'^2+y'^2+z'^2=R^2,$$

so that (x, y) is the stereographic projection of the point (x', y', z') on a sphere of radius R.

Obtaining the differentials dx', dy', dz', we find

$$ds^2=dx'^2+dy'^2+dz'^2=\frac{4R^2k}{(x^2+y^2+k)^2}(dx^2+dy^2).$$

Hence
$$R^2=-\mu^2.$$

Hence when k is positive and μ purely imaginary and $=iR$, the geometry is the same as that upon a sphere of radius

R, and the representation is by taking the stereographic projection.

When k is negative the sphere has an imaginary radius, but such an imaginary sphere can be conformly represented (by an imaginary transformation) upon a real surface of constant negative curvature, such as the surface of revolution of the tractrix about its asymptote (the pseudosphere).[1]

When k is zero μ must be infinite and the sphere becomes a plane.

Let $2\mu\sqrt{-k}=p$.

Then $$ds=\frac{p}{x^2+y^2}\sqrt{dx^2+dy^2}=\frac{p}{r^2}\sqrt{dr^2+r^2d\theta^2}.$$

By the transformation $r'=\frac{p}{r}$, $\theta'=\theta$

this becomes $ds^2=dr'^2+r'^2d\theta'^2=dx'^2+dy'^2$.

Hence when k is zero the geometry is the same as that upon a plane, *i.e.* Euclidean geometry, and the representation is by inversion, or reciprocal radii.

§ 20. Let us now return to the consideration of motions and investigate the nature of the general displacement of a rigid plane figure.[2] In ordinary space the general displacement of a rigid plane figure is equivalent to a rotation about a definite point, and this again is equivalent to two successive reflexions in two straight lines through the point. Now the operation which corresponds to reflexion in a straight line is inversion in an orthogonal circle. The formulæ for inversion in the circle

$$z\bar{z}+\bar{p}z+p\bar{z}-k=0,$$

which is any circle cutting $z\bar{z}+k=0$ orthogonally, are

$$\frac{x'+g}{x+g}=\frac{y'+f}{y+f}=\frac{g^2+f^2+k}{(x+g)^2+(y+f)^2}=\frac{(x'+g)^2+(y'+f)^2}{g^2+f^2+k}$$

[1] Cf. Darboux, *Théorie des surfaces*, vii., chap. xi. Also Klein, *Nichteuklidische Geometrie, Vorlesungen.*

[2] Cf. Weber u. Wellstein, *Encyklopädie der Elementar-Mathematik* (2. Aufl. Leipzig, 1907), Bd. 2, Abschn. 2. Also, Klein u. Fricke, *Vorlesungen über die Theorie der automorphen Functionen* (Leipzig, 1897), Bd. 1.

or, using complex numbers,

$$z+p=\frac{(p\bar{p}+k)(z'+p)}{(\bar{z}'+\bar{p})(z'+p)}.$$

Whence $$z=\frac{k-p\bar{z}'}{\bar{z}'+\bar{p}}.$$

A second inversion in the circle

$$z\bar{z}+\bar{q}z+q\bar{z}-k=0$$

gives $$z=\frac{(k+p\bar{q})z''-k(p-q)}{(\bar{p}-\bar{q})z''+(k+\bar{p}q)}.$$

This will not hold when the circle of inversion is a straight line, $\theta=\phi$. Here inversion becomes reflexion and the formula is

$$z=z'e^{2i(\theta-\phi)}=\bar{z}'e^{2i\phi}.$$

This combined with an inversion gives

$$z=\frac{-\bar{p}z''+k}{z''+p}e^{2i\phi}.$$

Now these transformations are always of the general form

$$z=\lambda\frac{\alpha z'-k\beta}{\bar{\beta}z'+\bar{\alpha}}, \text{ where } |\lambda|=1.$$

In fact, this transformation is always of one or other of the two forms $$z=z'e^{2i\phi}$$

(when $\beta=0$) or $$z=\frac{-\bar{p}z'+k}{z'+p}e^{2i\phi}$$

(by dividing above and below by $\bar{\beta}$).

Hence *the general displacement of a plane figure is equivalent to a pair of inversions in two orthogonal circles.*

§ 21. In the general transformation there are always two points which are unaltered, for if $z'=z$ we have the quadratic equation

$$\bar{\beta}z^2+(\bar{\alpha}-\lambda\alpha)z+k\lambda\beta=0.$$

These form the centre of rotation, and the circles with these points as limiting points are the paths of the moving points.

There are three kinds of motions according as the roots of this quadratic are real, equal, or imaginary, or according as

the centre of rotation is real, upon the fundamental circle, or imaginary. The first case is similar to ordinary rotation. In the second the paths are all circles touching the fundamental circle. In the third the paths all cut the fundamental circle; one of these paths is an orthogonal circle, the other paths are the equidistant curves; the motion is a translation along a fixed line.

§ 22. It would appear that the representation by circles is a sort of generalisation of the Cayley-Klein representation, since a straight line is a circle whose centre is at infinity. When the circles degenerate in this way, however, the fixed circle becomes the line infinity, and the geometry degenerates to Euclidean.

It is of interest to deduce the general Cayley-Klein representation from the circular one, but this cannot be done by a conformal transformation.

Abandoning the conformal representation, the transformation which changes circles orthogonal to $x^2+y^2+k=0$ into straight lines is

$$\theta'=\theta, r'=\frac{2pr}{r^2-k}.$$

The points (r, θ), $(-\frac{k}{r}, \theta)$ are both represented by the same point, so that this transformation gives a (1, 1) correspondence between the pairs of real points which are inverse with respect to the circle $x^2+y^2+k=0$ and the points which lie within the circle $x^2+y^2+\frac{p^2}{k}=0$, since for real values of r, $r'^2<-\frac{p^2}{k}$. Every point upon the circle $r^2+k=0$ is thus to be considered double. To a pair of imaginary points corresponds a point outside the new fixed circle. Any circle, not orthogonal, is transformed into a conic having contact with the circle $kr^2+p^2=0$ at the two points which correspond to the intersections of the circle with the fixed circle $r^2+k=0$.

In fact, any curve in the r'-plane which cuts the fixed circle

at a finite angle is represented in the r-plane by a curve cutting the fixed circle orthogonally, and any curve in the r-plane which cuts the fixed circle at a finite angle other than a right angle corresponds in the r'-plane to a curve touching the fixed circle.

Let the equation of a curve in the r'-plane be $f(r', \theta')=0$.

Then $$\frac{d\theta'}{dr'}=-\frac{df}{dr'}\Big/\frac{df}{d\theta'}.$$

But $$\frac{df}{dr'}=\frac{df}{dr}\cdot\frac{dr}{dr'}=-\frac{(r^2-k)^2}{2p(r^2+k)}\cdot\frac{df}{dr}, \text{ and } \frac{df}{d\theta'}=\frac{df}{d\theta}.$$

Therefore $$\frac{d\theta'}{dr'}=-\frac{(r^2-k)^2}{2p(r^2+k)}\cdot\frac{d\theta}{dr}.$$

Hence when $r^2+k=0$, $\frac{d\theta'}{dr'}=\infty$ unless $\frac{d\theta}{dr}=0$, which proves the results.

§ 23. This transformation receives its simplest expression through the medium of the sphere.

Let a point Q be projected stereographically into P and centrally upon the same plane or a parallel plane into P' (Fig. 2).

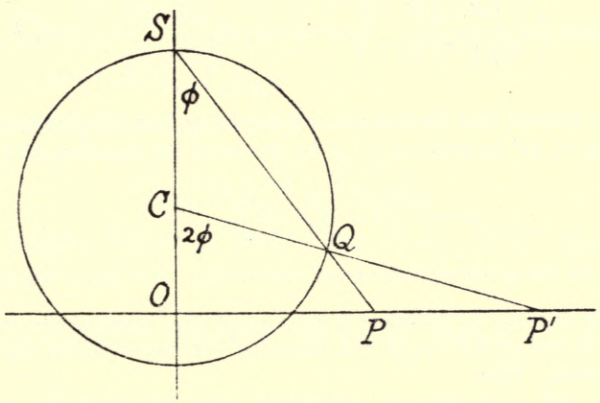

FIG. 2

Then $$\theta'=\theta,$$

and $r=OP=OS\tan\phi=c\tan\phi$, $r'=OP'=OC\tan 2\phi=c'\tan 2\phi$,

therefore $$r'=\frac{2cc'r}{c^2-r^2},$$

which agrees with the former equation if $c^2=k$ and $cc'=-p$, so that $c'^2=\frac{p^2}{k}=k'$, say.

Hence as the representation by circles corresponds to stereographic projection, the representation by straight lines corresponds to central projection.

The transformation from the sphere to the plane is in this case given by the equations

$$\frac{x}{x'}=\frac{y}{y'}=\frac{\sqrt{k'}}{z'}=\frac{1}{R}\sqrt{x^2+y^2+k'},$$

where $$x'^2+y'^2+z'^2=R^2.$$

Then [1] $$ds^2=dx'^2+dy'^2+dz'^2=R^2\frac{k'(dx^2+dy^2)+(ydx-xdy)^2}{(x^2+y^2+k')^2}.$$

§ 24. To determine the distance and angle functions in this representation we have first the relation between the angles from § 22,

$$\tan\phi'=-\tan\phi.\frac{(r^2-k)^2}{2p(r^2+k)}.\frac{r'}{r}=-\tan\phi.\frac{r^2-k}{r^2+k}=-\tan\phi.\sqrt{\frac{k'}{r'^2+k'}}$$

[1] It may be noticed that the line-element can be expressed in terms of x', y' alone Thus expressing z', dz' in terms of x', y' by means of the equation $x'^2+y'^2+z'^2=R^2$, we have

$$ds^2=\frac{R^2(dx'^2+dy'^2)-(y'dx'-x'dy')^2}{R^2-x'^2-y'^2}.$$

Here x', y', $\frac{z'}{R}$ are the so-called Weierstrass' coordinates. Let the position of a point P on the sphere be fixed by its distances ξ, η from two fixed great circles intersecting at right angles at Ω, and let $\Omega P=\rho$, all the distances being measured on the sphere along arcs of great circles. Then

$$x'=R\sin\frac{\xi}{R},\quad y'=R\sin\frac{\eta}{R},\quad z'=R\cos\frac{\rho}{R}.$$

On the pseudosphere the circular functions become hyperbolic functions. (See Killing, *Die nichteuklidischen Raumformen*, Leipzig, 1885, p. 17.)

where ϕ is the angle which the tangent at P to the curve $f(r, \theta)=0$ makes with the initial line.

Draw the tangents $P'T_1$, $P'T_2$ from P' to the circle (Fig. 3)

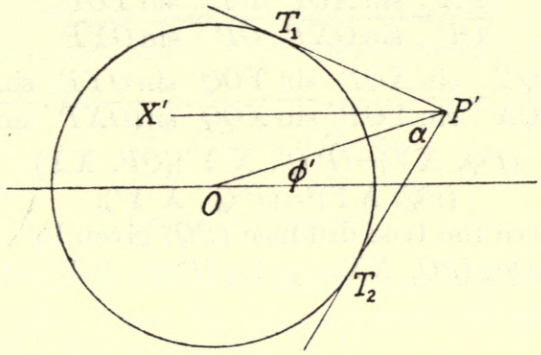

FIG. 3

and let $\angle OP'T_1=OP'T_2=\alpha$. Also draw $P'X'$ parallel to the x-axis. Then

$$\tan\alpha=\sqrt{\frac{-k'}{r'^2+k'}}=-i\frac{\tan\phi'}{\tan\phi}.$$

Therefore

$$e^{2i\phi}=\frac{\sin(\alpha-\phi')}{\sin(\alpha+\phi')}=\frac{\sin X'P'T_1}{\sin X'P'T_2}\cdot\frac{\sin OP'T_2}{\sin OP'T_1}$$
$$=P'(X'O,\ T_1T_2).$$

Thus the true angle ϕ is given by

$$\phi=\frac{i}{2}\log(OX',\ T_1T_2).$$

Hence the angle between two lines $P'X'$, $P'Y'$ through P' is given by

$$\frac{i}{2}\log(OY',\ T_1T_2)-\frac{i}{2}\log(OX',\ T_1T_2)=\frac{i}{2}\log(X'Y',\ T_1T_2).$$

Next to determine the distance function; let P, Q become P', Q' (Fig. 4). The orthogonal circle $PQXY$ becomes a straight line $P'Q'X'Y'$, and OPP', OQQ', etc., are collinear since angles at O are unaltered.

We have then

$$(PQ)=\mu\log(PQ,\ XY)=\mu\log\left(\frac{PX}{PY}\cdot\frac{QY}{QX}\right).$$

But
$$\frac{PX}{OP}=\frac{\sin XOP}{\sin OXP},\quad \frac{PY}{OP}=\frac{\sin YOP}{\sin OYP}$$

and
$$\frac{PX}{PY}\cdot\frac{QY}{QX}=\frac{\sin XOP}{\sin YOP}\cdot\frac{\sin YOQ}{\sin XOQ}\cdot\frac{\sin OYP}{\sin OXP}\cdot\frac{\sin OXQ}{\sin OYQ}$$

i.e.
$$(PQ,\ XY)=(P'Q',\ X'Y')(QP,\ XY)$$

therefore
$$(PQ,\ XY)^2=(P'Q',\ X'Y').$$

Hence we have the true distance (PQ) given by

$$(PQ)=\mu\log(PQ,\ XY)=\tfrac{1}{2}\mu\log(P'Q',\ X'Y')=(P'Q').$$

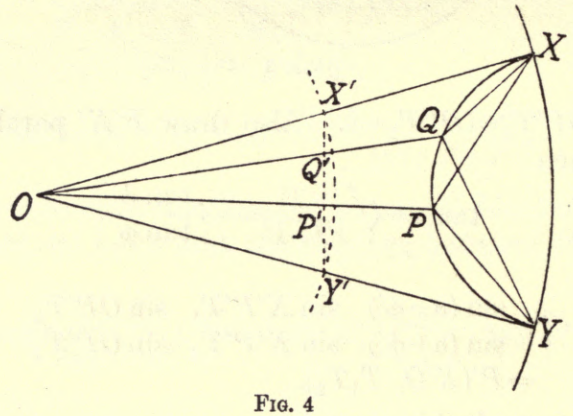

FIG. 4

Then the line-element can be obtained in a manner similar to that of § 17.

We find as before that $(PQ,\ XY)=1+\dfrac{XY}{PY\,.\,QX}\,.\,PQ$;

but in this case $PX\,.\,PY=x^2+y^2+k'$

and $XY^2=-4\{k'(dx^2+dy^2)+(ydx-xdy)^2\}/(dx^2+dy^2)$;

so that
$$ds^2=-\mu^2\,.\,\frac{k'(dx^2+dy^2)+(ydx-xdy)^2}{(x^2+y^2+k')^2}\,.$$

Comparing this with the expression in § 23 we find

$$R^2=-\mu^2.$$

§ 25. Finally, this representation may be transformed projectively (distances and angles being unaltered as they are functions of cross-ratios), and we get the usual generalised representation in which the fixed circle or absolute becomes any conic ; straight lines are represented by straight lines, and distances, and angles in circular measure, are expressed by the formulæ

$$(PQ)=\frac{\mu}{2}\log(PQ,\ XY)$$

$$(pq)=\frac{i}{2}\log(pq,\ xy)$$

where X, Y are the points in which the straight line PQ cuts the conic, and x, y are the tangents from the point of intersection of the lines p, q to the conic.

Geodesic Representation on Surfaces of Constant Curvature

§ 26. It has been seen that both the Cayley-Klein representation and the conformal representation by circles are derivable by projection from a sphere, real or imaginary, on which the non-Euclidean straight lines are represented by great circles. By Gauss' Theorem the sphere may be transformed, or limited portions of the surface may be deformed, into a surface of constant measure of curvature, in such a way that geodesics remain geodesics and are unaltered in length. The effect is that of bending without stretching ; the geometry therefore remains the same. To Beltrami [1] is due this representation of non-Euclidean geometry upon a surface of constant curvature, and it is the only representation in which distances and angles are represented unchanged.

§ 27. While this representation is of the first importance in non-Euclidean geometry, it has to be distinctly understood

[1] *Loc. cit.*, p. 5, foot-note 2.

that it is only a representation. A vast deal of misconception has grown around it. The following points have been most generally misunderstood:—

(1) There is an essential difference between Riemann's geometry and the geometry on the surface of a sphere.[1] The former is a true metrical geometry of two dimensions, and is no more dependent upon three dimensions[2] than ordinary geometry is on the 'fourth dimension.' The geometry on the surface of a sphere, on the other hand, is a body of doctrine forming a part of ordinary geometry of three dimensions.

(2) The fact that there is in ordinary space only one uniform real surface other than the plane has led certain critics[3] to reject Hyperbolic and Elliptic geometries as false and absurd, while they admit Spherical geometry only as a branch of ordinary geometry of three dimensions. This view is not so common now since the investigations of Pasch, Hilbert, and others on geometries defined by systems of axioms have become better known.

(3) The term 'curvature,' especially when extended to space of three dimensions, has given rise to much confusion, and has led to the notion that non-Euclidean geometry of

[1] Cf. P. Mansion, 'Sur la non-identité du plan riemannien et de la sphère euclidienne,' Bruxelles, *Ann. Soc. scient.*, 20 B (1896), a reply to Lechalas in the same volume. See also B. Russell, 'Geometry, non-Euclidean,' *Encycl. Brit.* (10th ed.), p. 669d.

[2] This statement must not be confused with the result that plane projective geometry, which is free from metrical considerations, and in which the Euclidean and non-Euclidean hypotheses are not distinguished, cannot be established completely without using space of three dimensions. The theorem of Desargues relating to perspective triangles, which is proved easily by projection in space of three dimensions, is incapable of deduction from the axioms of plane projective geometry alone. Thus there are two-dimensional but not three-dimensional non-Desarguesian geometries. In the same way the theorem of Pascal for a conic, or, in the special form, the theorem of Pappus, when the conic reduces to two straight lines, from which Desargues' theorem can be deduced, is incapable of deduction from the axioms of plane projective geometry alone. In this sense plane geometry is dependent upon three dimensions; but it is only necessary to make some additional assumption, Pascal's theorem or an equivalent, in order to construct plane geometry without reference to three dimensions.

[3] Cf., *e.g.*, E. T. Dixon, *The Foundations of Geometry* (Cambridge, Bell, 1891), p. 140.

three dimensions necessarily implies space of four dimensions.[1] The truth is that Beltrami's representation, as he himself expressly states, breaks down when we pass to three dimensions, and it is necessary, in order to obtain an analogous representation, to introduce space of four dimensions. The geometry, however, is a true geometry of three dimensions, having its own axioms or assumptions, one of which is that there exists no point outside its space. The term 'curvature' is therefore without meaning. The constant K^2 which occurs in the Cayley-Klein formula, and which corresponds to the measure of curvature of the surface upon which the geometry may be represented, has been called on this account the measure of curvature of the space, but as this is so misleading the term is now generally replaced by 'space-constant.' When it is finite it gives a natural unit of length like the natural angular unit. In Elliptic geometry it may be replaced by the length of the complete straight line; in Hyperbolic geometry where K^2 is negative iK can be constructed as follows:[2]— Take two lines OA, OB at right angles, and draw $A'B'$ so that $A'B' \parallel OB$ and $B'A' \parallel OA$; then draw an arc OL of a limit-curve through O perpendicular to OA and $B'A'$; the arc $OL=iK$. Another natural unit based upon K is the area of the maximum triangle, which has all its angles zero, the limit being $-\pi K^2$.

(4) Confusion has also existed with regard to the comparison of spaces with different space-constants. As there can be no comparison between one line and another unless they are in the same space, it appears clear that it is meaningless to

[1] For example, S. Newcomb, 'Elementary Theorems relating to the Geometry of a Space of three Dimensions and of uniform positive Curvature in the Fourth Dimension,' *J. Math.*, Berlin, 83 (1877). Clifford attempted, playfully no doubt, but with a certain seriousness, to explain physical phenomena by periodic variations in the curvature of space (*Common-sense of the Exact Sciences*, chap. iv., § 19). Helmholtz also, by his popularisation of the results of Beltrami and Riemann, did a good deal to promulgate this view especially among philosophers. Cf. Russell, *loc. cit.*

[2] See Engel, Leipzig, *Ber. Ges. Wiss.*, 50 (1898), p. 190.

speak of different spaces of the same type but with different space-constants. It is exactly analogous to the obvious absurdity of speaking of spaces in which the total angle at a point is of various magnitudes. The angle may be represented by different numbers, 4, 360, 6·283 . . ., and so on, according to the arbitrary unit which is adopted; so long as we are dealing with one space this angle has a constant magnitude, but there is no possibility of comparing magnitudes when the objects are in different spaces. There are the three types of space according as K^2 is positive, zero, or negative. For elliptic geometry, for example, different positive values of K^2 mean simply a different choice of the arbitrary unit of length. (Cf. Russell and Whitehead, *Encycl. Brit.* (11th ed.), article 'Geometry,' section vi., 'Non-Euclidean Geometry,' p. 725d.)

Representation of Projective Metric by Apparent Magnitude as seen from a View-Point

§ 27. It has been indicated in § 6 that spherical and elliptic geometries of two dimensions are capable of representation as the geometries of a bundle of straight lines or a bundle of rays through a fixed point. The former is the geometry of 'visual space,' the latter is the geometry of the infinitely distant elements. For a plane or a line through the fixed point gives a line or a point at infinity, and the angle between two lines is represented by the distance between the infinitely distant points. The absolute for the geometry at infinity is the imaginary circle at infinity.

'Visual geometry' is a two-dimensional geometry exactly analogous to this except for the existence of antipodal points; *i.e.* as every astronomer knows, Visual geometry is the same as Spherical geometry. It is the geometry which would be constructed by a being endowed only with monocular vision and without powers of locomotion.

§ 28. A somewhat analogous representation for geometry of three dimensions has been devised by E. M'Clintock and modified by W. W. Johnson.[1]

We have seen that the geometry on the surface of a sphere gives, by central projection on any plane, a representation by straight lines with the Cayley-Klein projective metric. On every plane, with the exception of those through the centre of the sphere, a definite metric is thus established. To eliminate these exceptional planes M'Clintock proceeds in this way. A fixed point O is taken in space, and the metric on any plane through this point is defined to be that upon a tangent plane to the sphere in which O corresponds to the point of contact. The metric upon any other plane at a distance r from O is then defined to be that upon a plane parallel to the tangent plane, and at a distance r from it on the opposite side from the centre, the foot of the perpendicular from O corresponding to the foot of the perpendicular from the centre of the sphere.

This procedure is modified in an elegant manner by Johnson. Assume a 'central point' O and a linear magnitude c corresponding to the radius of the sphere; then the projective measure of a segment is its apparent magnitude viewed from a point P at a distance c from O measured in a direction perpendicular to the plane through the given line and O. All lines in this plane have the same view-point, or pair of view-points.

Consider any line l, and let the plane through O perpendicular to l cut l in A. Draw a circle with centre A passing through P, P'. Any point on this circle will also be a view-point for the line l. Hence a line has a view-circle.

Consider any plane α, and take a line l in it. Construct the view-circle of l, whose centre is A and whose plane passes

[1] E. M'Clintock, 'On the non-Euclidean Geometry,' New York, *Bull. Amer. Math. Soc.*, 2 (1892), 21-33. W. W. Johnson, 'A Case of non-Euclidean Geometry,' *ibid.*, 158-161.

through O. Let A' be the foot of the perpendicular from O upon a, and let OA' cut the view-circle of l in Q, Q'. Then, in Fig. 5, $A'Q^2=AQ^2-p'^2=AP^2-p^2+d^2=c^2+d^2$. Hence the points Q, Q' depend only upon the position of the plane and are independent of the line l. Q, Q' therefore form a pair of view-points for all lines in the plane. Again, for all planes through l the view-points lie on the view-circle of l, and the

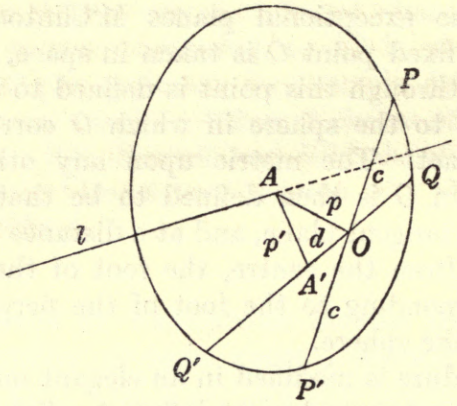

FIG. 5

metric upon any line is the same, independently of the plane in which it may be conceived to lie.

The measure of an angle is then defined to be its apparent magnitude viewed from the view-point of its plane.

This representation is only suitable for Elliptic geometry. In Hyperbolic geometry c^2 is negative, and the radius of a view-circle is real only if $p^2>-c^2$; the view-points of a plane are real only if $d^2>-c^2$. Hence for all lines and planes which do not cut the real sphere with centre O and radius $\sqrt{-c}$ the geometry is elliptic, and these lines and planes correspond to ideal or ultra-spatial elements. For the lines and planes which cut the sphere and which correspond to actual elements the view-points are imaginary.

Representation by a Net of Conics

§ 30. We have next to consider a generalisation of the representation by circles, in which the circles are replaced by conics. The conics must form a linear system depending upon two parameters, *i.e.* a *net*. Further, to make the system correspond as closely as possible to the system of circles, which are conics passing through the two circular points, we shall suppose the net to be a special net passing through two fixed points, X, Y. The general equation of a system of conics passing through two fixed points may be written

$$S+(px+qy+rz)\alpha=0$$

where S is an expression of the second degree, α of the first degree, and p, q, r are parameters. The parameters must be connected by a linear homogeneous relation, hence the variable line $px+qy+rz=0$ must pass through a fixed point Z. Taking XYZ as the triangle of reference, the equation reduces to the form

$$axy+bz^2+z(px+qy)=0$$

where p, q are now the two parameters of the net.

The conic degenerates to two lines, one through X, the other through Y, if $pq=ab$. It degenerates to the line $z=0$ and a line $y=mx$, passing through Z, for infinite values of the parameters.

§ 31. Consider a line $y=mx$ through Z. This cuts a conic of the system where

$$amx^2+bz^2+zx(p+qm)=0.$$

By choosing p and q suitably it may be made to touch the conic. The condition for this is

$$(p+qm)^2=4abm.$$

Eliminating $p+qm$ we obtain

$$(amx^2+bz^2)^2=4abmz^2x^2,$$

or

$$(axy-bz^2)^2=0.$$

The locus of points of contact of tangents from Z to the

system is therefore a double conic, which touches ZX and ZY at X and Y.

Every line through Z is therefore cut in involution by the system of conics, and the double points of the involutions lie on the conic $axy=bz^2$. Further, on each conic of the system there is an involution formed by the pencil with vertex Z, and the double points of these involutions are the points of intersection of the conics with the conic $axy=bz^2$. We have, then, what we require, two absolute points on every conic which represents a straight line, and these absolute points lie on a fixed conic. We may therefore call the conic $axy=bz^2$ the Absolute.

§ 32. The conic

$$axy+bz^2+z(px+qy)=0$$

cuts the absolute where

$$(2axy)^2b=axy(px+qy)^2,$$

which gives $x=0$ or $y=0$ or

$$4abxy=(px+qy)^2.$$

According as the points of intersection are real, coincident, or imaginary, the conic represents a line with hyperbolic, parabolic, or elliptic metric. The condition that the points of intersection be coincident is

$$\Delta\equiv ab(ab+pq)=0.$$

If a or b vanishes all lines are parabolic.

When $a=0$ the absolute becomes a double line $z^2=0$, and every conic of the system breaks up into this line and a variable line $px+qy+bz=0$. The representation is then by straight lines, and if X, Y are an imaginary point-pair the geometry is Parabolic. If X, Y are the circular points the geometry is Euclidean, and the representation is identical.

When $b=0$ the absolute breaks up into two lines $x=0$, $y=0$, and every conic of the system passes through the three points X, Y, Z. If X, Y are an imaginary point-pair the geometry is again Parabolic, and if X, Y are the two circular points the representation is by circles passing through a fixed point.

If the absolute is not degenerate we may get lines of all three forms. If X, Y are real the absolute is real. We may suppose a, b, which are real, to have the same sign, then the conic represents an elliptic or a hyperbolic line according as $pq \lessgtr -ab$.

If X, Y are imaginary the triangle of reference has two imaginary vertices, but we may take as real triangle of reference a triangle self-conjugate with regard to the absolute. The equation of a conic of the system may then be written

$$\lambda x^2+\mu y^2+z^2+z(px+qy)=0$$

where λ, μ have the same sign, and the equation of the absolute, found by the same method as before, is

$$\lambda x^2+\mu y^2=z^2.$$

The absolute is therefore real or imaginary according as λ and μ are both positive or both negative.

The discriminant in this case is

$$\Delta \equiv p^2\mu+q^2\lambda-4\lambda\mu.$$

If λ, μ are both negative this is negative, and all lines are therefore elliptic when the absolute is imaginary.

The equation of a conic of the system may be written

$$\lambda(x+\frac{p}{2\lambda}z)^2+\mu(y+\frac{q}{2\mu}z)^2=\frac{\Delta}{4\lambda\mu}z^2.$$

Hence when λ and μ are both positive the conic is real only when $\Delta>0$, so that, when the absolute is real and X, Y are an imaginary pair, all real conics represent hyperbolic lines.

The following is a summary of the results :—

X, Y are imaginary, and the absolute is

(1) A real proper conic, with the point Z in its interior. Hyperbolic geometry.

(2) An imaginary conic. Elliptic geometry.

(3a) A double line XY. Parabolic geometry, with representation by straight lines.

(3b) A pair of imaginary lines ZX, ZY. Parabolic geometry, with representation by conics passing through Z.

When X, Y are real there are conics which represent hyperbolic, parabolic, and elliptic lines, and the measure of angle is hyperbolic.

When X, Y are coincident the measure of angle is parabolic.

§ 33. In the representation by circles the points X, Y are the circular points, while Z is the centre of the fixed circle. The general representation by conics in the case where X, Y are imaginary is, of course, at once obtainable by projection from the representation by circles. A real conic and a point inside it can always be projected into a circle and its centre. All that is necessary is to make the centre correspond to the given point and the line infinity to the polar of this point. From this we deduce at once the distance and angle functions in this representation.

The angle between two lines is $\frac{1}{2}i$ times the logarithm of the cross-ratio of the pencil formed by the tangents to the two conics at their point of intersection and the lines joining this point to X, Y.

Two points P, Q determine a conic cutting the absolute in U, V; the distance (PQ) is then μ times the logarithm of the cross-ratio (PQ, UV) of the four points on this conic.

A circle is represented by any conic passing through X, Y.

§ 34. In the circular representation we saw that motions are represented by pairs of inversions in orthogonal circles. In the representation by conics there is an analogous transformation. Any line through Z is cut in involution by the system of conics, the double points being on the absolute. The transformation by which any point is transformed into its conjugate is a quadric inversion.[1] The conics of the system are transformed into themselves by such a transformation, while the points of the absolute are invariant.

To find the equations of transformation, take XYZ as triangle of reference, and write the equation of the absolute

[1] On quadric inversion see C. A. Scott, *Modern Analytical Geometry*, pp. 230-236.

$xy=z^2$. P is found from P' as the intersection of ZP' with the polar of P'. The polar of $P'(x'y'z')$ is

$$xy'+x'y=2zz',$$

and the equation of ZP' is

$$xy'=x'y.$$

Hence
$$x:y:z=\frac{1}{y'}:\frac{1}{x'}:\frac{1}{z'}.$$

§ 35. We may similarly establish a quadric inversion with regard to any conic of the system. Let the conic cut the

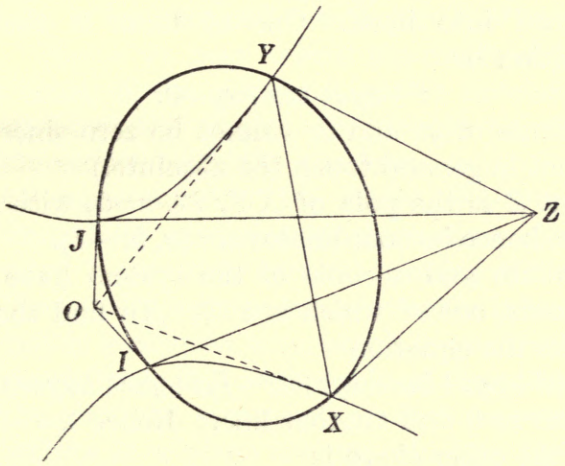

FIG. 6

absolute in I, J. Draw the tangents at I, J to the absolute, cutting in O. Then O is to be taken as the centre of inversion. The same point O is obtained by drawing the tangents to the conic at X, Y. (See Fig. 6, where the absolute is the ellipse and for clearness X, Y are taken to be real.) Hence XY is the polar of O. The conic and the absolute with the points Z and O simply exchange rôles, and the conic is left invariant by the transformation, while the absolute is transformed into itself.

The inverse of a conic is in general a curve of the fourth degree, but if the conic passes through X, Y the inverse is also a conic passing through X, Y. In fact, taking OXY as the triangle of reference and representing the fixed conic by the equation $xy=z^2$, the equation of any conic passing through X, Y is

$$cz^2+fyz+gzx+hxy=0,$$

and this is transformed into

$$hz^2+fyz+gzx+cxy=0.$$

Also any conic whose equation is of the form

$$z^2+fyz+gzx+xy=0$$

is transformed into itself. One of these is the absolute. Let its equation be

$$z^2+ayz+bzx+xy=0.$$

(The coefficients of yz and zx cannot be zero since the fixed conic does not in general touch the absolute.)

The point Z is the pole of XY, *i.e.* $z=0$, with respect to the absolute, hence its coordinates are $(a, b, -1)$.

The absolute and a conic of the system have a pair of common chords, one of which is $z=0$. To find the other we have to make the equation

$$\lambda(z^2+ayz+bzx+xy)+cz^2+fyz+gzx+hxy=0$$

break up into $z=0$ and another line. Hence $\lambda=-h$, and the equation of the other chord is

$$(g-bh)x+(f-ah)y+(c-h)=0.$$

But this chord is the polar of Z with respect to the conic. The equation of the polar of Z is

$$(g-bh)x+(f-ah)y+(2c-ga-fb)=0.$$

Hence

$$ga+fb=h+c,$$

which is the condition which must be satisfied by the coefficients in order that the conic

$$cz^2+fyz+gzx+hxy=0$$

may be a conic of the system. Since the relation is symmetrical in c and h the inverse is also a conic of the system.

Hence by quadric inversion with regard to any conic of

the system the absolute is transformed into itself, and any conic of the system is transformed into a conic of the system. A single quadric inversion is thus analogous to a reflexion, while the general motion is produced by a pair of quadric inversions.

These results could also be obtained by projection, for quadric inversion, in the case where the points X, Y are imaginary, can be compounded of ordinary inversion in a circle and a collineation.

By a quadric inversion the pencil of lines passing through Z, which, together with the line XY, form a pencil of conics of the system, is transformed into a pencil of conics passing through O. Hence we may extend the result of § 31 and say that every conic of the system is cut in involution by any pencil of conics of the system, the double points being the points of intersection with the absolute.

Like the representation by circles, this representation admits of immediate extension to three dimensions. Planes are represented by quadric surfaces passing through a fixed conic, C. Two such quadrics intersect again in another conic. The linear metric is referred to an absolute quadric also passing through C, such that, if Z is the pole of the plane of C with respect to the absolute, any quadric which represents a plane cuts the absolute in a plane section, which is the polar of C with respect to the quadric.

Representation by Diametral Sections of a Quadric Surface

§ 36. We shall briefly describe one other representation, due to Poincaré.[1] In this representation straight lines are represented by diametral sections of a quadric surface.

[1] H. Poincaré, 'Sur les hypothèses fondamentales de la géométrie,' Paris, *Bull. Soc. math.*, **15** (1887), 203-216. Cf. also H. Jansen, 'Abbildung der hyperbolischen Geometrie auf ein zweischaliges Hyperboloid,' Hamburg, *Mitt. math. Ges.*, **4** (1909), 409-440.

Project the quadric stereographically, *i.e.* with the centre of projection O on the surface. The two generators through O give two fixed points X, Y, and any plane section is projected into a conic passing through X, Y. The points at infinity on the quadric project into a fixed conic, also passing through X, Y, and the pole of XY with respect to the fixed conic is a point Z, which is the projection of the centre C of the quadric. The tangents at infinity, *i.e.* the asymptotes, of a diametral section, pass through C, and their projections therefore pass through Z. Hence the projection consists of the net of conics which we considered in the last section.

The angle and distance functions can therefore be deduced. At a point P a pencil is determined by the tangents to the diametral sections and the two generators, which correspond in the projection to the two lines passing through X, Y. The angle between the lines represented by the diametral sections is then proportional to the logarithm of the cross-ratio of this pencil. In a diametral section a range is determined by two points and the two points at infinity, which correspond in the projection to the intersections with the fixed conic. The distance between the two points is then proportional to the logarithm of the cross-ratio of this configuration on the diametral section. A circle corresponds in the projection to any conic passing through X, Y, *i.e.* it is represented by any plane section.

If the quadric is ruled the points X, Y are real and the measure of angle is hyperbolic; or parabolic if the quadric degenerates to a cone.

The geometry is Hyperbolic, Parabolic, or Elliptic according as the quadric is a hyperboloid of two sheets, an elliptic paraboloid, or an ellipsoid.

§ 37. If the quadric is projected from the centre, diametral sections become straight lines; the points at infinity give again a fixed conic, the section of the asymptotic cone; and any plane section projects into a conic having double contact

with the fixed conic, so that the representation is by the Cayley-Klein projective metric.

The close connection between the representation by diametral sections of a quadric surface and that by diametral sections of a sphere is now apparent.

There is an apparent gain in the generality of the representation if the centre of projection O be chosen arbitrarily. The tangent planes through O to the asymptotic cone project into two straight lines cutting in Z, the projection of the centre. These lines are tangents to the conic which corresponds to the points at infinity, and the points of contact are X, Y. A plane section projects into a conic passing through X, Y, and its asymptotes project into the tangents at the points of intersection with the fixed conic. For a diametral section these tangents pass through Z. Thus we obtain once more the same representation by a net of conics through two fixed points, and there is no gain in generality by this general projection.

The extension of this representation to non-Euclidean geometry of three dimensions requires Euclidean space of four dimensions. The representation is by diametral sections of a fixed quadratic variety, which must not be ruled, *i.e.* a tangent 3-flat must cut the variety in an imaginary cone. The geometry is Hyperbolic or Elliptic according as the variety cuts the 3-flat at infinity in a real or an imaginary quadric.

DUNCAN M'LAREN YOUNG SOMMERVILLE

ON THE ALGEBRAICAL SOLUTION OF INDETERMINATE CUBIC EQUATIONS

PART I

§ 1. Theorem. If a particular non-zero solution of a homogeneous indeterminate cubic equation be known, then an algebraical solution can in general be found.

Let $$\phi(X_1, X_2, \ldots, X_n)=0 \qquad (1)$$
be a homogeneous indeterminate cubic in n variables $X_1, X_2, \ldots, X_n$, and let it have a particular non-zero solution, say
$$X_1=a_1, X_2=a_2, \ldots, X_n=a_n, \qquad (2)$$
so that $$\phi(a_1, a_2, \ldots, a_n)=0 \qquad (3)$$
where by hypothesis $a_1, a_2, \ldots a_n$ do not all vanish.

Now make the substitutions
$$X_1=x_1r+a_1, X_2=x_2r+a_2, \ldots, X_n=x_nr+a_n \qquad (4)$$
and equation (1) becomes on expansion in powers of r
$$A_3r^3+A_2r^2+A_1r+\phi(a_1, a_2, \ldots a_n)=0, \qquad (5)$$
where A_3, A_2, A_1 are homogeneous integral functions of $x_1, x_2, \ldots, x_n$ of the third, second, and first degree, respectively.

The term in equation (5) independent of r vanishes by (3). The coefficient of r can be made to vanish by solving the equation
$$A_1=0 \qquad (6)$$
which being linear and homogeneous in $x_1, x_2, \ldots x_n$ can always be solved. Let the value so found for x_n say in terms of $x_1, x_2, \ldots x_{n-1}$ be substituted in A_2 and A_3, which will in general be finite functions of $x_1, x_2, \ldots, x_{n-1}$. The equation (5) is then identically satisfied by taking
$$r=-A'_2/A'_3 \qquad (7)$$
where A'_2, A'_3 are what A_2, A_3 become when x_n is expressed in terms of $x_1, x_2, \ldots, x_{n-1}$ by (6). The values of x_n and r, given

by (6) and (7), when substituted in (4), furnish the solution. Moreover, since the original equation $\phi(X_1, X_2, \ldots, X_n)=0$ is homogeneous, we can make the solution integral by multiplying the value of each of the roots given by (4) by the algebraical quantity A'_3 and by the numerical quantity which is introduced from the fact that the value of x_n is in general fractional; and since A'_2, A'_3 are integral homogeneous functions of $x_1, x_2, \ldots, x_{n-1}$, it follows that the solution presents the roots $X_1, X_2, \ldots, X_n$ as rational integral homogeneous functions of the third degree in $n-1$ variables $x_1, x_2, \ldots, x_{n-1}$.

If any of the quantities $a_1, a_2, \ldots, a_n$ instead of being numerical are arbitrary literal quantities, they will appear in the final values for $X_1, X_2, \ldots, X_n$ as variables, and will therefore alter the number of variables in, and the degree of, the final solution.

§ 2. If the equation $\phi=0$ is not homogeneous, and integral solutions be required, some care in the choice of particular solutions and in a suitable preparation of ϕ must be exercised to secure this end. An example of this is given in Question 6 below.

§ 3. This process is naturally open to failure when the equation under consideration admits only of solutions of a certain type. An example of this is the equation $x^3+y^3=2z^3$, which admits only of solutions of the type (k, k, k), or of the type $(k,-k, o)$,[1] and the application of the method furnishes only the same type of solution.

§ 4. It is to be remarked that if $\phi=0$ is a homogeneous cubic in three variables, the solution does not present the roots as functions of two variables in accordance with § 1; for $\phi=0$ may be regarded as a non-homogeneous cubic in two independent variables, and the solution will not present the roots as functions of even one unknown, but is again particular, and being in general fractional and distinct from the

[1] Euler, *Elements of Algebra*, part ii. chap. xv. § 247. Fourth edition. 1828.

assumed solution, in this way an infinite number of fractional solutions is found. The reason why the method fails to give an algebraical solution in this latter case is because equation (6) gives a linear and homogeneous relation between x_1 and x_2, and when it has been satisfied equation (5) is no longer an indeterminate one between r and x_1 but gives a unique determinate value for the single variable formed by their product $x_1 r$. Thus both values of the variables X_1, X_2 in (4) are particular. (See Question 5 below.)

Again, if an indeterminate equation of any degree can, by regarding certain of the variables as constant, be considered as an indeterminate cubic in two or more variables of which a particular solution is known, then another solution can be found, but since it will present the roots as functions of the variables which were for the time regarded as mere coefficients, it is clear that the solution will always be algebraical.[1]

Finally, if $\phi(X_1, X_2, \ldots, X_n)=0$ be an indeterminate cubic of which a particular solution is known, namely,

$$X_1=a_1,\ X_2=a_2,\ \ldots,\ X_n=a_n,$$

and if $\psi(Y_1, Y_2, \ldots, Y_r)$ be a function of the third degree, not necessarily homogeneous but containing no constant term, of r variables $Y_1, Y_2, \ldots, Y_r$, none of which are identical with any of $X_1, X_2, \ldots, X_n$ except those whose value for the particular solution of $\phi=0$ is zero, then the equation

$$\psi(Y_1, Y_2, \ldots, Y_r)+\phi(X_1, X_2, \ldots, X_n)=0$$

can be solved. For it is evidently an indeterminate cubic in $n+r$ variables having the particular solution

$$Y_1=Y_2=\ldots=Y_r=0,\ X_1=a_1,\ X_2=a_2,\ \ldots,\ X_n=a_n.$$

An example of this is given in Question 2 below.

§ 5. It is to be further remarked that if $\phi=0$ is a quadratic indeterminate, then equation (5) does not contain $A_3 r^3$, and solutions are obtained by simply taking $r=-A_1/A_2$, and

[1] See Part II, Section I: On the Algebraical Solution of the Equation

$$P_1^4+P_2^4+P_3^4+\ldots+P^4_{n+2}=P'^4_1+P'^4_2+\ldots P'^4_{r+2}:$$

Question 1.

these as before may be integralised if the equation be homogeneous. On the other hand, if $\phi=0$ be an indeterminate biquadratic, in at least four unknowns, then equation (5) will contain an additional term A_4r^4 where A_4 is homogeneous and of the fourth degree in the unknowns. When equation (6) is solved and the value of one of the variables so determined is substituted in A_2, $A'_2=0$ becomes an indeterminate quadratic in at least three unknowns. If, therefore, rational solutions of $A_2=0$ can be found, equation (5) is solved by taking $r=-A_3/A_4$, and it is clear that in general the solutions of the final equation $\phi=0$ will be numerical or algebraical according as those of A_2 are algebraical or numerical. It is, however, exceptional for the subsidiary equation $A_2=0$ to yield rational solutions.[1]

§ 6. The above convenient method for the solution of indeterminate cubics will be illustrated by some typical examples. From these it will appear that there are few problems, if any, in indeterminate cubics to which it is inapplicable, or in which the results furnished are less general than those of another process.

QUESTION 1. Solve algebraically the equation

$$P_0^3=P_1^3+P_2^3+\ \ldots\ +P_n^3 \qquad (A)$$

(i) Let $n=3$, so that we have to solve

$$P_0^3=P_1^3+P_2^3+P_3^3 \qquad (1)$$

Here we may take as our particular solution

$$P_0=P_1=\lambda,\ P_2=-P_3=\mu \qquad (2)$$

Making then the substitutions

$$P_0=x_0r+\lambda,\ P_1=x_1r+\lambda,\ P_2=x_2r+\mu,\ P_3=x_3r-\mu, \qquad (3)$$

equation (1) takes the form

$$(x_0r+\lambda)^3=(x_1r+\lambda)^3+(x_2r+\mu)^3+(x_3r-\mu)^3$$

or, on expansion

$$(x_0^3-x_1^3-x_2^3-x_3^3)r^3+3(\lambda x_0^2-\lambda x_1^2-\mu x_2^2+\mu x_3^2)r^2 +3(\lambda^2x_0-\lambda^2x_1-\mu^2x_2-\mu^2x_3)r=0. \qquad (4)$$

[1] See the writer's paper: 'On the Algebraical Solution of the Indeterminate Equation $\lambda X^4+\mu Y^4=\nu Z^4+\rho V^4$': in course of preparation.

To make the coefficient of r vanish we may take

$$x_0=(\lambda^2 x_1+\mu^2 x_2+\mu^2 x_3)/\lambda^2 \tag{5}$$

and equation (4) is then satisfied by taking

$$r=3(\lambda x_1^2+\mu x_2^2-\mu x_3^2-\lambda x_0^2)/(x_0^3-x_1^3-x_2^3-x_3^3) \tag{6}$$

Substituting the value of x_0 from (5) in (6) we derive

$$r=\frac{3\lambda^3(\lambda^4 x_1^2+\lambda^3\mu x_2^2-\lambda^3\mu x_3^2-(\lambda^2 x_1+\mu^2 x_2+\mu^2 x_3^2)}{(\lambda^2 x_1+\mu^2 x_2+\mu^2 x_3)^3-\lambda^6(x_1^3+x_2^3+x_3^3)} \tag{7}$$

If we now put $\Delta\equiv(\lambda^2 x_1+\mu^2 x_2+\mu^2 x_3)^3-\lambda^6(x_1^3+x_2^3+x_3^3)$ (8)

equations (3) take the form

$$\left.\begin{aligned}
\Delta\cdot P_0&=\Delta(x_0 r+\lambda)=\lambda(\lambda^2 x_1+\mu^2 x_2+\mu^2 x_3)^3-\lambda^7(x_1^3+x_2^3+x_3^3)\\
&+3\lambda(\lambda^2 x_1+\mu^2 x_2+\mu^2 x_3)\{\lambda^4 x_1^2+\lambda^3\mu(x_2^2-x_3^2)-(\lambda^2 x_1+\mu^2 x_2+\mu^2 x_3)^2\}\\
\Delta\cdot P_1&=\Delta(x_1 r+\lambda)=\lambda(\lambda^2 x_1+\mu^2 x_2+\mu^2 x_3)^3-\lambda^7(x_1^3+x_2^3+x_3^3)\\
&+3\lambda^3 x_1\{\lambda^4 x_1^2+\lambda^3\mu x_2^2-\lambda^3\mu x_3^2-(\lambda^2 x_1+\mu^2 x_2+\mu^2 x_3)^2\}\\
\Delta\cdot P_2&=\Delta(x_2 r+\mu)=\mu(\lambda^2 x_1+\mu^2 x_2+\mu^2 x_3)^3-\lambda^6\mu(x_1^3+x_2^3+x_3^3)\\
&+3\lambda^3 x_2\{\lambda^4 x_1^2+\lambda^3\mu x_2^2-\lambda^3\mu x_3^2-(\lambda^2 x_1+\mu^2 x_2+\mu^2 x_3)^2\}\\
\Delta\cdot P_3&=\Delta(x_3 r-\mu)=\lambda^6\mu(x_1^3+x_2^3+x_3^3)-\mu(\lambda^2 x_1+\mu^2 x_2+\mu^2 x_3)^3\\
&+3\lambda^3 x_3\{\lambda^4 x_1^2+\lambda^3\mu x_2^2-\lambda^3\mu x_3^2-(\lambda^2 x_1+\mu^2 x_2+\mu^2 x_3)^2\}
\end{aligned}\right\} \tag{9}$$

As equation (1) is homogeneous, (9) is the integralised form of its algebraical solution and presents the roots as rational functions of five variables x_1, x_2, x_3, λ, μ ; of the third degree in x_1, x_2, x_3, the ninth in x_1, x_2, x_3, μ, and the tenth in x_1, x_2, x_3, λ, μ.

As a numerical example, $x_1=x_2=\lambda=1, -x_3=\mu=2$ gives, on removal of the common factor, $3^3+4^3+5^3=6^3$, the lowest solution which exists.

(ii) Let $n=4$, so that we have to solve

$$P_0^3=P_1^3+P_2^3+P_3^3+P_4^3 \tag{1'}$$

Here we may take as our particular solution

$$P_0=P_1=\lambda,\ P_2=-P_3=\mu,\ P_4=0 \tag{2'}$$

Making then the substitutions

$$P_0=x_0 r+\lambda,\ P_1=x_1 r+\lambda,\ P_2=x_2 r+\mu,\ P_3=x_3 r-\mu,\ P_4=x_4 r, \tag{3'}$$

equation (1′) takes the form

$$(x_0 r+\lambda)^3=(x_1 r+\lambda)^3+(x_2 r+\mu)^3+(x_3 r-\mu)^3+(x_4 r)^3$$

or on expansion

$$(x_0^3-x_1^3-x_2^3-x_3^3-x_4^3)r^3+3(x_0^2\lambda-x_1^2\lambda-x_2^2\mu+x_3^2\mu)r^2 +3(x_0\lambda^2-x_1\lambda^2-x_2\mu^2-x_3\mu^2)r=0 \quad (4')$$

To make the coefficient of r vanish we may take

$$x_0=(\lambda^2x_1+\mu^2x_2+\mu^2x_3)/\lambda^2 \quad (5')$$

and equation (4′) is then satisfied by taking

$$r=3(\lambda x_1^2+\mu x_2^2-\mu x_3^2-\lambda x_0^2)/(x_0^3-x_1^3-x_2^3-x_3^3-x_4^3) \quad (6')$$

Substituting the value of x_0 from (5′) in (6′) we derive

$$r=\frac{3\lambda^3\{\lambda^4x_1^2+\lambda^3\mu x_2^2-\lambda^3\mu x_3^2-(\lambda^2x_1+\mu^2x_2+\mu^2x_3)^2\}}{(\lambda^2x_1+\mu^2x_2+\mu^2x_3)^3-\lambda^6(x_1^3+x_2^3+x_3^3+x_4^3)} \quad (7')$$

Now put $\Delta'\equiv(\lambda^2x_1+\mu^2x_2+\mu^2x_3)^3-\lambda^6(x_1^3+x_2^3+x_3^3+x_4^3)$ (8′)

and equations (3) take the form

$$\left.\begin{aligned}
\Delta'P_0&=\Delta'(x_0r+\lambda)=\lambda(\lambda^2x_1+\mu^2x_2+\mu^2x_3)^3-\lambda^7(x_1^3+x_2^3+x_3^3+x_4^3)\\
&+3\lambda(\lambda^2x_1+\mu^2x_2+\mu^2x_3)\{\lambda^4x_1^2+\lambda^3\mu x_2^2-\lambda^3\mu x_3^2-(\lambda^2x_1+\mu^2x_2+\mu^2x_3)^2\}\\
\Delta'P_1&=\Delta'(x_1r+\lambda)=\lambda(\lambda^2x_1+\mu^2x_2+\mu^2x_3)^3-\lambda^7(x_1^3+x_2^3+x_3^3+x_4^3)\\
&+3\lambda^3x_1\{\lambda^4x_1^2+\lambda^3\mu x_2^2-\lambda^3\mu x_3^2-(\lambda^2x_1+\mu^2x_2+\mu^2x_3)^2\}\\
\Delta'P_2&=\Delta'(x_2r+\mu)=\mu(\lambda^2x_1+\mu^2x_2+\mu^2x_3)^3-\lambda^6\mu(x_1^3+x_2^3+x_3^3+x_4^3)\\
&+3\lambda^3x_2\{\lambda^4x_1^2+\lambda^3\mu x_2^2-\lambda^3\mu x_3^2-(\lambda^2x_1+\mu^2x_2+\mu^2x_3)^2\}\\
\Delta'P_3&=\Delta'(x_3r-\mu)=-\mu(\lambda^2x_1+\mu^2x_2+\mu^2x_3)^3+\lambda^6\mu(x_1^3+x_2^3+x_3^3+x_4^3)\\
&+3\lambda^3x_3\{\lambda^4x_1^2+\lambda^3\mu x_2^2-\lambda^3\mu x_3^2-(\lambda^2x_1+\mu^2x_2+\mu^2x_3)^2\}\\
\Delta'P_4&=\Delta'x_4r=3\lambda^3x_4\{\lambda^4x_1^2+\lambda^3\mu x_2^2-\lambda^3\mu x_3^2-(\lambda^2x_1+\mu^2x_2+\mu^2x_3)^2\}
\end{aligned}\right\} \quad (9')$$

As before (9′) is the integralised form of the algebraical solution of (1′), and presents the roots as rational functions of six variables x_1, x_2, x_3, x_4, λ, μ ; the roots being of the third degree in x_1, x_2, x_3, x_4, the ninth in x_1, x_2, x_3, x_4, μ, and the tenth in x_1, x_2, x_3, x_4, λ, μ.

As a numerical example $x_1=x_2=x_3=x_4=\lambda=\mu=1$ gives

$$49^3=47^3+24^3+1^3+1^3.$$

(iii) In general, the assumptions [1]

[1] Cf. *Mathematics from the Educational Times*, New Series, vol. iv. No. 15225.

$$(x_0r)^3=(x_1r+\lambda)^3+(x_2r-\lambda)^3+(x_3r+\mu)^3+(x_4r-\mu)^3+\ \ldots \\ +(x_{2m-1}r+\rho)^3+(x_{2m}r-\rho)^3$$

$$(x_0r+\lambda)^3=(x_1r+\lambda)^3+(x_2r+\mu)^3+(x_3r-\mu)^3+(x_4r+\nu)^3+\ \ldots \\ +(x_{2m}r+\rho)^3+(x_{2m+1}r-\rho)^3$$

are sufficient to give algebraical solutions of equation (A) for the two cases $n=2m$ and $n=2m+1$. In the former case the roots will be functions of the $2m$ quantities $x_1, x_2, \ldots, x_{2m}$, and of the m quantities $\lambda, \mu, \ldots, \rho$; in the latter the roots will be functions of the $2m+1$ quantities $x_1, x_2, \ldots, x_{2m+1}$, and of the $m+1$ quantities $\lambda, \mu, \ldots, \rho$.

QUESTION 2. Solve the equation

$$xy(x-y)=\lambda z^3 \tag{1}$$

knowing a particular solution, say $x=a$, $y=b$, $z=c$ so that

$$ab(a-b)=\lambda c^3 \tag{2}$$

Put $x=x_1r+a$, $y=x_2r+b$, $z=x_3r+c$, (3)

and (1) on expansion and rearrangement becomes

$$(x_1x_2\overline{x_1-x_2}-\lambda x_3{}^3)r^3+(x_1-x_2\ \overline{bx_1+ax_2}+\overline{a-b}x_1x_2-3\lambda cx_3{}^2)r^2 \\ +(ab\ \overline{x_1-x_2}+\overline{a-b}\ \overline{ax_2+bx_1}-3\lambda c^2x_3)r=0 \tag{4}$$

Hence, making the coefficient of r vanish by taking

$$x_3=(ab\ \overline{x_1-x_2}+\overline{a-b}\ \overline{ax_2+bx_1})/3\lambda c^2, \tag{5}$$

equation (4) is satisfied by taking

$$r=\frac{(x_1-x_2)(bx_1+ax_2)+(a-b)x_1x_2-3\lambda cx_3{}^2}{\lambda x_3{}^3-x_1x_2(x_1-x_2)}$$

$$=\frac{-9ab(a-b)(a^2-ab+b^2)(bx_1-ax_2)^2}{b^3(2a-b)^3x_1{}^3-3ab^2(5a^3-6a^2b+2b^3)x_1{}^2x_2+3a^2b(2a^3-6ab^2+5b^3)x_1x_2{}^2-a^3(2b-a)^3x_2{}^3} \tag{6}$$

on substituting the value of x_3 given by (5) and replacing λc^3 by $ab\ (a-b)$ from (2).

Hence, if we call the denominator of r, Δ, we find, finally,

$$\left.\begin{aligned}\Delta x&=(x_1r+a)=a(2b-a)^3(bx_1-ax_2)^3\\ \Delta y&=(x_2r+b)=b(2a-b)^3(bx_1-ax_2)^3\\ \Delta z&=(x_3r+c)=-(a+b)(2a-b)(2b-a)(bx_1-ax_2)^3\end{aligned}\right\}\text{(B)}$$

which, it is to be remarked, is not an algebraical solution, but

gives a second solution when one is known. Thus if $\lambda=6$, then $x=3$, $y=2$, $z=1$ is a known solution, and (B) gives another solution $x=128$, $y=5$, $z=20$, from which we may derive a third, and so on *ad infinitum.*

If, on the other hand, the original equation had been

$$\mu_1 V_1^3+\mu_2 V_2^3+ \ldots +\mu_n V_n^3+xy(x-y)=\lambda z^3, \qquad (1')$$

in which $\mu_1, \mu_2, \ldots, \mu_n$ are given coefficients and $V_1, V_2, \ldots, V_n$ variables, since $V_1=V_2= \ldots =V_n=0$, $x=a$, $y=b$, $z=c$ is, by hypothesis, a particular solution, the substitutions (3) and $V_s=t_s r$ would have led to an equation in no wise differing from (4) except that the term $\Sigma\mu_s t_s^3$ would have appeared in the coefficient of r^3. Hence, subtracting $27\lambda^2c^6(\Sigma\mu_s t_s^3)$ from the denominator of r in (6), it is clear that the final solution of (1′), omitting the common denominator, would be

$$\left.\begin{aligned} V_s&=-9ab(a-b)(a^2-ab+b^2)X^2t_s,\\ x&=a(2b-a)^3X^3-27a^3b^2(a-b)^2\Sigma\mu_s t_s^3,\\ y&=b(2a-b)^3X^3-27a^2b^3(a-b)^2\Sigma\mu_s t_s^3,\\ z&=-(a+b)(2a-b)(2b-a)X^3-27a^2b^2c(a-b)^2\Sigma\mu_s t_s^3, \end{aligned}\right\} (A')$$

where X is written for bx_1-ax_2, and this solution is obviously algebraical.

Thus if we put $n=1$, $\mu_1=5$, the equation

$$5V^3+xy(x-y)=6z^3$$

which has the obvious particular solution $V=0$, $x=3$, $y=2$, $z=1$, has the algebraical solution

$$\begin{aligned} V&=-378X^2t,\\ x&=3X^3-14580t^3,\\ y&=128X^3-9720t^3,\\ z&=-20X^3-4860t^3. \end{aligned}$$

Thus $X=4$, $t=1$ gives the solution

$$V=1512,\ x=3597,\ y=382,\ z=1535.$$

QUESTION 3. Solve the equation

$$xy(x^2-y^2)=u^2+2v^2, \qquad (1)$$

knowing a particular solution say $x=a$, $y=b$, $u=c$, $v=d$.

This equation is of the fourth degree in x, y, u, v, but by putting $y=b$ it becomes $\quad bx(x^2-b^2)=u^2+2v^2 \qquad (2)$

which is an indeterminate cubic in x, u, v having the particular solution $x=a, u=c, v=d$. Hence, to find an algebraical solution, we put $x=x_1r+a,\ u=x_2r+c,\ v=x_3r+d$ (3)
and (2) on expansion and rearrangement becomes

$$(bx_1^3)r^3+(3abx_1^2-x_2^2-2x_3^2)r^2 + (\overline{3a^2b-b^3}x_1-2c_1x_2-4dx_3)r=0. \quad (4)$$

Hence, making the coefficient of r vanish by taking

$$x_3=(\overline{3a^2b-b^3}x_1-2cx_2)/4d \quad (5)$$

equation (4) is satisfied by taking

$$r=(x_2^2+2x_3^2-3abx_1^2)/bx_1^3$$
$$=\frac{[(3a^2b-b^3)^2-24abd^2]x_1^2-4c(3a^2b-b^3)x_1x_2+4(c^2+2d^2)x_2^2}{8bd^2x_1^3}$$

on substituting the value of x_3 given by (5).

Hence, we find

$$\left.\begin{aligned}
x&=[\{(3a^2b-b^3)^3-16abd^2\}x_1^3-4c(3a^2b-b^3)x_1^2x_2\\
&\qquad+4(c^2+2d^2)x_1x_2^2]/8bd^2x_1^3,\\
u&=[8bcd^2x_1^3+\{(3a^2b-b^3)^2-24abd^2\}x_1^2x^2-4c(3a^2b-b^3)x_1x_2^2\\
&\qquad+4(c^2+2d^2)x_2^3]/8bdx_1^3,\\
v&=[\{(3a^2b-b^3)^3-24abd^2(3a^2b-b^3)+32bd^4\}x_1^3\\
&\quad-6c\{(3a^2b-b^3)^2-8abd^2\}x_1^2x_2+4(3a^2b-b^3)(3c^2+2d^2)x_1x_2^2\\
&\qquad-8c(c^2+2d^2)x_2^3]/32bd^3x_1^3.
\end{aligned}\right\} \quad (6)$$

For example, as a particular solution of (2), we may take

$$a=2,\ b=1,\ c=2,\ d=1. \quad (7)$$

Substituting these values in (6), we obtain, finally, the algebraical solution

$$x=(89x_1^2-88x_1x_2+24x_2^2)/8x_1^2, \qquad y=1,$$
$$u=(16x_1^3+73x_1^2x_2-88x_1x_2^2+24x_2^3)/8x_1^3,$$
$$v=(835x_1^3-1260x_1^2x_2+616x_1x_2^2-96x_2^3)/32x_1^3.$$

Hence we derive the following solutions, on integralising,

x_1	x_2	x	y	u	v
2	3	11	8	7	17
1	1	25	8	19	10

and these appear to be along with (7) the three smallest solutions which exist.

QUESTION 4. Find n rational-sided right-angled triangles, such that the algebraical sum of given rational multiples of their area is zero.

If the sides of the *rth* triangle are $x_r^2+a_r^2$, $x_r^2-a_r^2$, $2x_ra_r$, and λ_r is the given multiple of its area, we have evidently to solve

$$\lambda_1x_1a_1(x_1^2-a_1^2)+\lambda_2x_2a_2(x_2^2-a_2^2)+ \ . \ . \ . \ +\lambda_rx_ra_r(x_r^2-a_r^2)+ \ . \ . \ . \ +\lambda_nx_na_n(x_n^2-a_n^2)=0.$$

But this is evidently an indeterminate cubic in x_1, x_2, . . . x_r, . . . x_n, having the particular solution $x_1=a_1$, $x_2=a_2$, . . ., $x_r=a_r$, . . ., $x_n=a_n$. Hence an algebraical solution can be found.

QUESTION 5. Solve the equation

$$\lambda x^3+\mu y^3=1, \tag{1}$$

knowing a particular solution say $x=a$, $y=b$.

Putting $x=x_1r+a$, $y=y_1r+b$ (2), equation (1) becomes on expansion and rearrangement

$$(\lambda x_1^3+\mu y_1^3)r^3+3(\lambda ax_1^2+\mu by_1^2)r^2+3(\lambda a^2x_1+\mu b^2y_1)r=0 \tag{3}$$

Hence, making the coefficient of r vanish by taking

$$x_1=-(\mu b^2/\lambda a^2)y_1 \tag{4}$$

equation (3) is satisfied by taking

$$r=-3(\lambda ax_1^2+\mu by_1^2)/(\lambda x_1^3+\mu y_1^3)=-3\lambda a^3b/(\lambda a^3-\mu b^3)y_1. \tag{5}$$

Now since $x_1=-(\mu b^2/\lambda a^2)y_1$, and equation (5) gives merely a particular value of ry_1, it is clear that the values of x and y obtained from (2) will also be particular, viz. :

$$x=a(1+\mu b^3)/(\lambda a^3-\mu b^3), \ y=-b(1+\lambda a^3)/(\lambda a^3-\mu b^3). \tag{6}$$

In fact it is clear from the above and the solution of the first part of Question 2, that no greater generality would have been obtained by starting with the equation

$$\lambda X^3+\mu Y^3=\nu Z^3 \tag{7}$$

knowing the particular solution $X=a$, $Y=b$, $Z=c$.

For if in (6) we replace λ, μ, a, b by λ/ν, μ/ν, a/c, b/c respectively we shall obtain for (7) that if

$$\lambda a^3+\mu b^3=\nu c^3, \tag{8}$$

then $$\lambda X^3+\mu Y^3=\nu Z^3,$$

where $X=a(\mu b^3+\nu c^3)$, $Y=-b(\lambda a^3+\nu c^3)$, $Z=c(\lambda a^3-\mu b^3)$. (9)

For example, if the equation were

$$5X^3+6Y^3=Z^3,$$

then $a=-1$, $b=1$, $c=1$; $\lambda=5$, $\mu=6$, $\nu=1$, and consequently

$$X=-7,\ Y=4,\ Z=-11.$$

From this solution we may proceed to derive a third, and so on *ad infinitum.*

Cor. If in (8) we put $\lambda=\mu=\nu$, we derive that if

$$a^3+b^3=c^3$$

then [1] $$a^3(b^3+c^3)^3-b^3(c^3+a^3)^3=c^3(a^3-b^3)^3.$$

QUESTION 6. Express 5, 17, and 41 algebraically, each as the sum of five integral cubes.[2]

Taking the case of 5 first, since $5=5^3+2^3-4^3-4^3-0^3$, if we assume

$$5=(\xi-4)^3+(a\xi-4)^3+(-a\xi+2)^3+(b\xi)^3+(-b\xi+5)^3 \tag{1}$$

it is clear that, on expansion, the coefficient of ξ^3 will be unity, while the constant term disappears. If, therefore, we can make the coefficient of ξ vanish by expressing both a and b integrally in terms of some unknown, then we shall obtain an integral algebraical value for ξ which will render (1) an identity. Now (1) on expansion is

$$\xi^3+3(-4-2a^2+5b^2)\xi^2+3(16+12a-25b)\xi=0. \tag{2}$$

Hence to make the coefficient of ξ vanish we must have $25b=12a+16$, and this is done integrally by taking $a=25t+7$, $b=12t+4$. Substituting these values in (2), we find for the required value of ξ

$$1590t^2+660t+66.$$

[1] This result is due to Tait. See Chrystal's *Algebra*, part i. chap. xiv., Ex. xx. No. 2.

[2] Cf. *Mathematics from the Educational Times*, New Series, vol. iv. No. 15225.

Hence, finally, substituting these values of a, b, ξ in (1), we find the identity

$$5\equiv(1590t^2+660t+62)^3+(39750t^3+27630t^2+6270t+458)^3$$
$$-(39750t^3+27630t^2+6270t+460)^3+(19080t^3+14280t^2$$
$$+3432t+264)^3-(19080t^3+14280t^2+3432t+259)^3.$$

Thus $t=0$ gives

$$5\equiv 62^3+458^3-460^3+264^3-259^3,$$

while $t=-1$ gives

$$5\equiv 992^3-17932^3+17930^3-7968^3+7973^3.$$

By a similar process we obtain

$$17\equiv-(108t^2-48t+4)^3+(864t^3-816t^2+240t-22)^3$$
$$-(540t^3-456t^2+126t-13)^3+(540t^3-456t^2+126t-9)^3$$
$$-(864t^3-816t^2+240t-21)^3,$$

and $41\equiv-(246t^2-264t+76)^3+(1968t^3-3096t^2+1680t-310)^3$
$$-(1968t^3-3096t^2+1680t-311)^3+(738t^3-1284t^2$$
$$+762t-157)^3-(738t^3-1284t^2+762t-159)^3.$$

$t=0$, and $t=1$ give respectively

$$17\equiv-4^3-22^3+13^3-9^3+21^3,$$
$$\equiv-64^3+266^3-197^3+201^3-267^3,$$

and
$$41\equiv-76^3-310^3+311^3-157^3+159^3,$$
$$\equiv-58^3+242^3-241^3+59^3-57^3.$$

Part II

For the purposes of Diophantine Analysis, biquadratic equations may be divided into two classes according as they do or do not admit of representation, by a perfectly general transformation of their variables, as indeterminate cubics. Thus, for example, the equation

$$P_1^4+P_2^4=P'_1{}^4+P'_2{}^4$$

by the perfectly general transformation $P_1=x+y$, $P_2=u-v$, $P'_1=x-y$, $P'_2=u+v$, becomes

$$(x+y)^4+(u-v)^4=(x-y)^4+(u+v)^4$$

i.e.

$$x^3y+xy^3=u^3v+uv^3,$$

which is an indeterminate cubic in x and u; while, on the other hand, the equation

$$P_0^4=P_1^4+P_2^4+\ \ldots\ +P_n^4$$

does not seem capable, by a perfectly general transformation of its variables, of being represented as an indeterminate cubic in any number of variables. From what has been already shown,[1] it is clear that the former class of equations admits of an algebraic solution (at least when the number of variables exceeds 2) by a process universally applicable, and it is to this class the present paper is confined, though the methods of solution will not be restricted to that already given. The biquadratic equations of the second class require special artifices for their solution and a separate paper will be devoted to them.[2]

[1] In the writer's paper, Part I.

[2] Viz., Part III.

SECTION I—On the algebraical solution of the equation

$$P_1^4+P_2^4+\ \ldots\ +P_{n+2}^4=P'_1{}^4+P'_2{}^4+\ \ldots\ +P'_{r+2}{}^4.$$

§ 1. Before attempting to solve this equation for all values of n and r, it will be convenient first to give solutions for a few particular values of n and r.

QUESTION 1. Solve in integers the equation

$$P_1^4+P_2^4=P'_1{}^4+P'_2{}^4. \tag{1}$$

Let $P_1=z_1+z_3$, $P_2=z_2-z_4$, $P'_1=z_1-z_3$, $P'_2=z_2+z_4$ and the equation becomes

$$z_1^3z_3+z_1z_3^3=z_2^3z_4+z_2z_4^3 \tag{2}$$

This is an indeterminate cubic in z_1 and z_2 and if any particular solution is known, another can be found, but as it presents the new roots as functions of the coefficients z_3 and z_4, it will be an algebraical solution. Thus, putting $z_1=x_1r+y_1$, $z_2=x_2r+y_2$, (2) becomes

$$(x_1r+y_1)^3z_3+(x_1r+y_1)z_3^3=(x_2r+y_2)^3z_4+(x_2r+y_2)z_4^3$$

or, on expansion and rearrangement,

$$\begin{aligned}(x_1^3z_3-x_2^3z_4)r^3+3(x_1^2y_1z_3-x_2^2y_2z_4)r^2+(3x_1y_1^2z_3+x_1z_3^3-3x_2y_2^2z_4\\ -x_2z_4^3)r+(y_1^3z_3+y_1z_3^3)-(y_2^3z_4+y_2z_4^3)=0.\end{aligned} \tag{3}$$

To make the term independent of r vanish, we must have

$$(y_1^3z_3+y_1z_3^3)=(y_2^3z_4+y_2z_4^3)$$

which is equivalent to knowing a particular solution of (1) since it may be written

$$(y_1+z_3)^4+(y_2-z_4)^4=(y_1-z_3)^4+(y_2+z_4)^4, \tag{4}$$

and to satisfy this we may evidently take

$$y_1+z_3=-y_2-z_4,\ y_1-z_3=y_2-z_4,\ i.e.\ y_1=-z_4,\ y_2=-z_3 \tag{5}.$$

In order to make the coefficient of r in (3) vanish, we must take

$$x_1(3y_1^2z_3+z_3^3)-x_2(3y_2^2z_4+z_4^3)=0$$

i.e.

$$\begin{aligned}x_2&=[(3y_1^2z_3+z_3^3)/(3y_2^2z_4+z_4^3)]x_1\\ &=[z_3(3z_4^2+z_3^2)/z_4(3z_3^2+z_4^2)]x_1\end{aligned} \tag{6}$$

on substituting for y_1, y_2 their values given by (5).

Equation (3) is now identically satisfied by taking

$$r=3(x_2^2y_2z_4-x_1^2y_1z_3)/(x_1^3z_3-x_2^3z_4)$$

$$=\frac{3[-(3z_4^2+z_3^2)^2z_3^3+(3z_3^2+z_4^2)^2z_4^2z_3](3z_3^2+z_4^2)z_4}{[-(3z_3^2+z_4^2)^3z_4^2z_3+(3z_4^2+z_3^2)^3z_3^3]x_1}$$

$$=\frac{3[z_4^3+3z_4z_3^2+z_3^3+3z_4^2z_3][z_4^3+3z_4z_3^2-z_3^3-3z_4^2z_3](3z_3^2+z_4^2)z_4}{[27(z_4^6z_3^2-z_3^6z_4^2)+27(z_4^4z_3^4-z_3^4z_4^4)+9(z_4^2z_3^6-z_4^6z_3^2)+(z_3^8-z_4^8)]x_1}$$

$$=\frac{3(z_4+z_3)^3(z_4-z_3)^3(3z_3^2+z_4^2)z_4}{x_1(z_4^4-z_3^4)[27z_4^2z_3^2-9z_4^2z_3^2-z_4^4-z_3^4]}=\frac{3z_4(z_4^2-z_3^2)^2(3z_3^2+z_4^2)}{x_1(z_4^2+z_3^2)(18z_4^2z_3^2-z_4^4-z_3^4)};$$

say $dr=3z_4(z_4^2-z_3^2)^2(3z_3^2+z_4^2)$,

where $d=x_1(z_4^2+z_3^2)(18z_4^2z_3^2-z_4^4-z_3^4)$

Hence $dz_1=x_1\cdot dr+dy_1=3x_1z_4(z_4^2-z_3^2)^2(3z_3^2+z_4^2)$

$$+x_1z_4(z_4^2+z_3^2)(18z_4^2z_3^2-z_4^4-z_3^4)$$

$$=x_1z_4[3z_4^6+3z_4^4z_3^2-15z_4^2z_3^4+9z_3^6-z_4^6+17z_4^4z_3^2$$

$$+17z_4^2z_3^4-z_3^6]$$

$$=2x_1z_4[z_4^6+10z_4^4z_3^2+z_4^2z_3^4+4z_3^6],$$

and by symmetry

$$dz_2=2x_1z_3[z_3^6+10z_3^4z_4^2+z_3^2z_4^4+4z_4^6].$$

Hence $dP_1=d(z_1+z_3)=x_1[2z_4(z_4^6+10z_4^4z_3^2+z_4^2z_3^4+4z_3^6)$

$$-z_3(z_3^2+z_4^2)(18z_4^2z_3^2-z_4^4-z_3^4)]$$

$$dP_2=d(z_2-z_4)=x_1[2z_3(z_3^6+10z_3^4z_4^2+z_3^2z_4^4+4z_4^6)$$

$$+z_4(z_4^2+z_3^2)(18z_4^2z_3^2-z_4^4-z_3^4)]$$

$$dP'_1=d(z_1-z_3)=x_1[2z_4(z_4^6+10z_4^4z_3^2+z_4^2z_3^4+4z_3^6)$$

$$+z_3(z_3^2+z_4^2)(18z_4^2z_3^2-z_4^4-z_3^4)]$$

$$dP'_2=d(z_2+z_4)=x_1[2z_3(z_3^6+10z_3^4z_4^2+z_3^2z_4^4+4z_4^6)$$

$$-z_4(z_3^2+z_4^2)(18z_4^2z_3^2-z_4^4-z_3^4)].$$

Thus, finally, we have the algebraic identity [1]

$$[2x^7+x^6y+20x^5y^2-17x^4y^3+2x^3y^4-17x^2y^5+8xy^6+y^7]^4$$

$$+[x^7-8x^6y-17x^5y^2-2x^4y^3-17x^3y^4-20x^2y^5+xy^6-2y^7]^4$$

$$=[2x^7-x^6y+20x^5y^2+17x^4y^3+2x^3y^4+17x^2y^5+8xy^6-y^7]^4$$

$$+[x^7+8x^6y-17x^5y^2+2x^4y^3-17x^3y^4+20x^2y^5+xy^6+2y^7]^4$$

on writing x for z_4 and y for z_3.

For example $x=1$, $y=2$ gives $76^4+1203^4=1176^4+653^4$,

and $x=1$, $y=3$ gives $133^4+134^4=158^4+59^4$.

[1] This identity is due to Euler (*Commentationes Arithmeticæ*, vol. ii. p. 289), who obtained it by a different method.

§ 2. The equation $P_1^4+P_2^4=P'_1{}^4+P'_2{}^4+k$ is always soluble whatever be the value of k, provided a particular solution be known. For by putting $P_1=x+y$, $P_2=u-v$, $P'_1=x-y$, and $P'_2=u+v$ it becomes

$$8x^3y+8xy^3=8u^3v+8uv^3+k$$

which is an indeterminate cubic in x and u. We proceed to solve the case where $k=P'_3{}^4-P_3^4$.

QUESTION 2. Solve the equation

$$P_1^4+P_2^4+P_3^4=P'_1{}^4+P'_2{}^4+P'_3{}^4 \tag{1}$$

First method. We may assume

$$(x_1r+a)^4+(x_2r+b)^4+(x_3r+c)^4=(x_1r+d)^4+(x_2r+e)^4+(x_3r+f)^4 \tag{2}$$

where by hypothesis

$$a^4+b^4+c^4=d^4+e^4+f^4. \tag{3}$$

On expansion and rearrangement (2) becomes

$$4(\overline{a-d}x_1^3+\overline{b-e}x_2^3+\overline{c-f}x_3^3)r^3+6(\overline{a^2-d^2}x_1^2+\overline{b^2-e^2}x_2^2+\overline{c^2-f^2}x_3^2)r^2+4(\overline{a^3-d^3}x_1+\overline{b^3-e^3}x_2+\overline{c^3-f^3}x_3)r=0. \tag{4}$$

To make the coefficient of r vanish we must take

$$x_3=\{(a^3-d^3)x_1+(b^3-e^3)x_2\}/(f^3-c^3). \tag{5}$$

Equation (4) is then satisfied by taking

$$r=-\frac{3[(a^2-d^2)x_1^2+(b^2-e^2)x_2^2+(c^2-f^2)x_3^2]}{2[(a-d)x_1^3+(b-e)x_2^3+(c-f)x_3^3]}$$

$$=-\frac{3(f^3-c^3)[\{(a^2-d^2)x_1^2+(b^2-e^2)x_2^2\}(f^3-c^3)(f^2+fc+c^2)-(c+f)\{(a^3-d^3)x_1+(b^3-e^3)x_2\}^2]}{2[\{(a-d)x_1^3+(b-e)x_2^3\}(f^3-c^3)^2(f^2+fc+c^2)-\{(a^3-d^3)x_1+(b^3-e^3)x_2\}^3]},$$

on substituting for x_3 its value given by (5). These values of x_3 and r when substituted in (2) render it an identity and constitute a solution which is clearly algebraical.

We may satisfy equation (3) in several ways. Thus we may put

$$d=-a,\ f=b,\ e=c.$$

Hence $$x_3=[2a^3x_1+(b^3-c^3)x_2]/(b^3-c^3),$$

and

$$r=\frac{-3(b^3-c^3)[(b^2-c^2)(b^3-c^3)(b^2+bc+c^2)x_2^2-(b+c)\{2a^3x_1+(b^3-c^3)x_2\}^2]}{2[\{2ax_1^3+(b-c)x_2^3\}(b^3-c^3)^2(b^2+bc+c^2)-\{2a^3x_1+(b^3-c^3)x_2\}^3]}.$$

As a particular case put $x_1=-x_2=a=c=1$, $b=2$, so that

$$x_3=-5/7,\ r=-21/13.$$

Hence substituting in (2) the foregoing values we obtain

$$8^4+28^4+47^4=34^4+34^4+41^4.$$

In the same way we may derive other algebraical solutions by putting $d=\pm b$, $e=\pm c$, $f=\pm a$, etc.

Second method. In the identity

$$(a+b)^4-(a-b)^4=8a^3b+8ab^3$$

replace a by x_1^4 and b by $2y_1^4$. Then

$$(x_1^4+2y_1^4)^4-(x_1^4-2y_1^4)^4=(2x_1^3y_1)^4+4(2x_1y_1^3)^4$$

i.e.

$$\left(\frac{x_1^4+2y_1^4}{2x_1y_1^3}\right)^4-\left(\frac{x_1^4-2y_1^4}{2x_1y_1^3}\right)^4-\left(\frac{x_1^2}{y_1^2}\right)^4$$
$$=\left(\frac{x_2^4+2y_2^4}{2x_2y_2^3}\right)^4-\left(\frac{x_2^4-2y_2^4}{2x_2y_2^3}\right)^4-\left(\frac{x_2^2}{y_2^2}\right)^4$$
$$= \quad . \quad . \quad . \quad .$$
$$=\left(\frac{x_n^4+2y_n^4}{2x_ny_n^3}\right)^4-\left(\frac{x_n^4-2y_n^4}{2x_ny_n^3}\right)^4-\left(\frac{x_n^2}{y_n^2}\right)^4=4 \qquad (1)$$

Taking the first only of these equations and integralising we have

$$\{x_2y_2^3(x_1^4+2y_1^4)\}^4+\{x_1y_1^3(x_2^4-2y_2^4)\}^4+\{2x_1y_1^3x_2^3y_2\}^4$$
$$=\{x_1y_1^3(x_2^4+2y_2^4)\}^4+\{x_2y_2^3(x_1^4-2y_1^4)\}^4+\{2x_2y_2^3x_1^3y_1\}^4 \qquad (2)$$

which is an identity of the kind required. Thus we have

x_1	x_2	y_1	y_2	$P_1^4+P_2^4+P_3^4=P'^4_1+P'^4_2+P'^4_3$
1	2	1	1	$3^4+7^4+8^4=1^4+2^4+9^4$
1	1	2	1	$8^4+16^4+33^4=4^4+24^4+31^4$

of which the former is the second smallest solution which exists, the smallest being $2^4+4^4+7^4=3^4+6^4+6^4$.

Cor. In equation (2) replace x_1, y_1, x_2, y_2 by their reciprocals and multiply each root by $x_1^4.y_1^4.x_2^4.y_2^4$. We thereby obtain

$$\{x_2^3y_2(y_1^4+2x_1^4)\}^4+\{x_1^3y_1(y_2^4-2x_2^4)\}^4+\{2x_1^3y_1x_2y_2^3\}^4$$
$$=\{x_1^3y_1(y_2^4+2x_2^4)\}^4+\{x_2^3y_2(y_1^4-2x_1^4)\}^4+\{2x_2^3y_2x_1y_1^3\}^4. \qquad (3)$$

Adding now corresponding sides of (2) and (3) and omitting the terms which are common to both sides we obtain

$$\{x_2y_2^3(x_1^4+2y_1^4)\}^4+\{x_1y_1^3(x_2^4-2y_2^4)\}^4+\{x_2^3y_2(y_1^4+2x_1^4)\}^4+\{x_1^3y_1(y_2^4-2x_2^4)\}^4$$
$$=\{x_1y_1^3(x_2^4+2y_2^4)\}^4+\{x_2y_2^3(x_1^4-2y_1^4)\}^4+\{x_1^3y_1(y_2^4+2x_2^4)\}^4+\{x_2^3y_2(y_1^4-2x_1^4)\}^4.$$

For example, $x_1=x_2=y_2=1$, $y_1=2$ gives

$$2^4+8^4+18^4+33^4=6^4+14^4+24^4+31^4.$$

Again, we have identically

$$(x_1^4+2y_1^4)^4-(x_1^4-2y_1^4)^4-(2x_1^3y_1)^4=4(2x_1y_1^3)^4$$
$$(x_2^4+2y_2^4)^4-(x_2^4-2y_2)^4-(2x_2^3y_2)^4=4(2x_2y_2^3)^4.$$

Multiplying corresponding sides of these equations together we obtain

$$\{(x_1^4+2y_1^4)(x_2^4+2y_2^4)\}^4+\{(x_1^4-2y_1^4)(x_2^4-2y_2^4)\}^4+\{4x_1^3x_2^3y_1y_2\}^4+\{2x_1^3y_1(x_2^4-2y_2^4)\}^4+\{2x_2^3y_2(x_1^4-2y_1^4)\}^4$$
$$=\{(x_2^4+2y_2^4)(x_2^4-2y_2^4)\}^4+\{(x_1^4+2y_1^4)(x_2^4-2y_2^4)\}^4+\{2x_2^3y_2(x_1^4+2y_1^4)\}^4+\{2x_1^3y_1(x_2^4+2y_2^4)\}^4+\{8x_1x_2y_1^3y_2^3\}^4.$$

which is an algebraical solution of the equation

$$P_1^4+P_2^4+P_3^4+P_4^4+P_5^4=P'_1{}^4+P'_2{}^4+P'_3{}^4+P'_4{}^4+P'_5{}^4.$$

Again, we have identically

$$\left(\frac{2x_1^4+y_1^4}{2x_1y_1^3}\right)^4-\left(\frac{2x_1^4-y_1^4}{2x_1y_1^3}\right)^4=4\left(\frac{x_1^2}{y_1^2}\right)^4+1,$$
$$\left(\frac{2x_2^4+y_2^4}{2x_2y_2^3}\right)^4-\left(\frac{2x_2^4-y_2^4}{2x_2y_2^3}\right)^4=4\left(\frac{x_2^2}{y_2^2}\right)^4+1.$$

Hence by subtraction we get

$$\left(\frac{2x_1^4+y_1^4}{2x_1y_1^3}\right)^4+\left(\frac{2x_2^4-y_2^4}{2x_2y_2^3}\right)^4-\left(\frac{2x_1^4-y_1^4}{2x_1y_1^3}\right)^4-\left(\frac{2x_2^4+y_2^4}{2x_2y_2^3}\right)^4=4\left(\frac{x_1^2}{y_1^2}\right)^4-4\left(\frac{x_2^2}{y_2^2}\right)^4.$$

Also $\left(\frac{2u^4+v^4}{u^3v}\right)^4-\left(\frac{2u^4-v^4}{u^3v}\right)^4-\left(\frac{2v^2}{u^2}\right)^4=4.$

If then we multiply corresponding sides of these last two equations together it is clear we shall obtain an identity of the form

$$P_1^4+P_2^4+\ \ldots\ +P_7^4=P'_1{}^4+P'_2{}^4+\ \ldots\ +P'_7{}^4.$$

The foregoing processes obviously admit of infinite combination and repetition.

Third method. We have identically

$$(x+y)^4+(x-y)^4+(2y)^4=2(x^2+3y^2)^2$$

and $$(u+v)^4+(u-v)^4+(2v)^4=2(u^2+3v^2)^2.$$

Hence we shall have

$$(x+y)^4+(x-y)^4+(2y)^4=(u+v)^4+(u-v)^4+(2v)^4 \qquad (1)$$

provided $$x^2+3y^2=u^2+3v^2 \qquad (2)$$

Now the most general solution of (2) is given by

$$\left.\begin{aligned} x&=[(3\lambda^2+1)v+(3\lambda^2-1)y]/2\lambda \\ u&=[(3\lambda^2-1)v+(3\lambda^2+1)y]/2\lambda \end{aligned}\right\}$$ where λ is arbitrary.

Hence the most general solution of (1) is given by

$$[(3\lambda^2+1)v+(3\lambda^2+2\lambda-1)y]^4+[(3\lambda^2+1)v+(3\lambda^2-2\lambda-1)y]^4+(4\lambda y)^4$$
$$=[(3\lambda^2+2\lambda-1)v+(3\lambda^2+1)y]^4+[(3\lambda^2-2\lambda-1)v+(3\lambda^2+1)y]^4+(4\lambda v)^4.$$

Thus $\lambda=-y=2$, $v=1$ gives

$$8^4+11^4+19^4=1^4+16^4+17^4.$$

Cor. 1. From the foregoing we may derive the solution of

$$(x_1+y_1)^4+(x_1-y_1)^4+(2y_1)^4=(x_2+y_2)^4+(x_2-y_2)^4+(2y_2)^4=\ \ldots$$
$$=(x_n+y_n)^4+(x_n-y_n)^4+(2y_n)^4.$$

For it is clear that the integer N, which is equal to the product

$$(a_1{}^2+3b_1{}^2)(a_2{}^2+3b_2{}^2)\ \ldots\ (a_r{}^2+3b_r{}^2),$$

is expressible in the form p^2+3q^2 in 2^{r-1} ways, and therefore as above $2N^2$ is expressible in the form $(x+y)^4+(x-y)^4+(2y)^4$ in the same number of ways.

In practice, where an arithmetical result merely is desired, it is easier to proceed as follows. Selecting the smallest

number, 7, which is of the form a^2+3b^2, since $7^4=49^2=(1^2+3\cdot4^2)^2$, we have

$$7^4[x^4+y^4+(x+y)^4]=2\left[\left(\frac{x-y}{2}\right)^2+3\left(\frac{x+y}{2}\right)^2\right]^2(1^2+3\cdot4^2)^2$$

$$=2\left[\left(\frac{x-y+12\overline{x+y}}{2}\right)^2+3\left(\frac{x+y-4\overline{x-y}}{2}\right)^2\right]^2$$

$$=(5x+8y)^4+(8x+3y)^4+(3x-5y)^4$$

i.e.
$$x^4+y^4+(x+y)^4=\left(\frac{3x-5y}{7}\right)^4+\left(\frac{5x+8y}{7}\right)^4+\left(\frac{8x+3y}{7}\right)^4 \quad (3)$$

Hence it is clear that we may replace x and y by $\frac{3x-5y}{7}$ and $\frac{5x+8y}{7}$ respectively (or by $\frac{3x-5y}{7}$ and $\frac{-8x-3y}{7}$ respectively, etc.) without altering the value of the left-hand side. Thus the next repetition gives

$$=\left(\frac{-16x-55y}{7^2}\right)^4+\left(\frac{55x+39y}{7^2}\right)^4+\left(\frac{39x-16y}{7^2}\right)^4, \quad (4)$$

and the process may be continued *ad infinitum*. Also we observe that we may interchange x and y without altering the left-hand side so that we have also

$$=\left(\frac{3y-5x}{7}\right)^4+\left(\frac{5y+8x}{7}\right)^4+\left(\frac{8y+3x}{7}\right)^4 \quad (5)$$

$$=\left(\frac{16y+55x}{7^2}\right)^4+\left(\frac{55y+39x}{7^2}\right)^4+\left(\frac{39y-16x}{7^2}\right)^4 \quad (6)$$

Thus for example if we put in (3), (4), (5), (6), $x=1$, $y=3$ we obtain

$$49^4+147^4+196^4=84^4+119^4+203^4=9^4+172^4+181^4$$
$$=28^4+161^4+189^4=101^4+103^4+204^4.$$

Cor. 2. Changing the sign of y in equation (3) we get

$$x^4+y^4+(x-y)^4=\left(\frac{3x+5y}{7}\right)^4+\left(\frac{5x-8y}{7}\right)^4+\left(\frac{8x-3y}{7}\right)^4 \quad (7)$$

Hence, subtracting (7) from (3) we derive

$$(7x+7y)^4+(3x+5y)^4+(8x-3y)^4+(5x-8y)^4=(7x-7y)^4 \\ +(3x-5y)^4+(8x+3y)^4+(5x+8y)^4$$

$x=y$ gives $3^4+5^4+8^4+14^4=2^4+11^4+13^4$;

$x=2$, $y=1$ gives $2^4+11^4+13^4+21^4=1^4+7^4+18^4+19^4$.

Cor. 3. In equation (3) put $x=5q-1$, $y=3q-2$ so that $3x-5y=7$, and we derive

$$(5q-1)^4+(3q-2)^4+(8q-3)^4=1^4+(7q-3)^4+(7q-2)^4 \qquad (8)$$

$$\therefore\ (5r-1)^4+(3r-2)^4+(8r-3)^4=1^4+(7r-3)^4+(7r-2)^4 \qquad (9)$$

Hence, subtracting (8) and (9) we have

$$(5q-1)^4+(3q-2)^4+(8q-3)^4+(7r-3)^4+(7r-2)^4=(5r-1)^4 \\ +(3r-2)^4+(8r-3)^4+(7q-3)^4+(7q-2)^4$$

$q=2$, $r=1$ gives $1^4+11^4+12^4=4^4+9^4+13^4$.

$q=3$, $r=2$ gives $4^4+9^4+13^4+18^4+19^4=7^4+11^4+12^4+14^4+21^4$.

§ 3. We shall now show how the equation

$$P_1^4+P_2^4+\ \ldots\ +P_{n+2}^4=P'_1{}^4+P'_2{}^4+\ \ldots\ +P'^4_{r+2}$$

may be solved by a single formula which holds for all values of n and r except the case $n=r=0$.

Let us first solve the equation

$$P_1^4+P_2^4=P'_1{}^4+P'_2{}^4+(2P)^4. \qquad (1)$$

Putting $P_1=a+b$, $P_2=c-d$, $P'_1=a-b$, $P'_2=c+d$, $P=ax$, (1) becomes

$$a^3b+ab^3=c^3d+cd^3+2a^4x^4 \qquad (2)$$

If now we take $d=ab^3/c^3$, (2) is satisfied by taking

$$a^3b=a^3b^9/c^8+2a^4x^4$$

i.e.
$$a=b(c^8-b^8)/2x^4c^8,$$

so that
$$d=b^4(c^8-b^8)/2x^4c^{11}.$$

Hence omitting the common denominator, and replacing x throughout by x/c^2, we have as a solution of (1)

$$P_1=bc^3(c^8+2x^4-b^8),\quad P_2=2c^4x^4-b^4c^8+b^{12},\quad P'_1=bc^3(c^8-2x^4-b^8),$$
$$P'_2=2c^4x^4+b^4c^8-b^{12},\quad 2P=2bc(b^8-c^8)x.$$

Thus we have the identity

$$[bc^3(b^8-c^8+2x^4)]^4+[2c^4x^4-b^8(c^8-b^8)]^4=[bc^3(c^8-b^8-2x^4)]^4 \\ +[2c^4x^4+b^8(c^8-b^8)]^4+[2bc(b^8-c^8)x]^4. \qquad (3)$$

For example $c=2$, $b=x=1$ gives

$$223^4+2056^4=287^4+1020^4+2024^4.$$

We may now deduce several results from (3).

(i) Replacing x^4 by X, equation (3) shows that every rational quantity X is expressible rationally in the form $P^4+Q^4-R^4-S^4$, in an infinity of ways, viz. :—

$$X=\left[\frac{c^2(c^8-b^8+2X)}{2(c^8-b^8)}\right]^4+\left[\frac{2c^4X-b^4(c^8-b^8)}{2bc(c^8-b^8)}\right]^4$$
$$-\left[\frac{c^2(c^8-b^8-2X)}{2(c^8-b^8)}\right]^4-\left[\frac{2c^4X+b^4(c^8-b^8)}{2bc(c^8-b^8)}\right]^4.$$

(ii) We may replace x^4 in (3) by $\Sigma_{n=1}^{n=n} x_n^4$, whence we have

$$[bc^3(c^8-b^8+2\Sigma x_n^4)]^4+[2c^4\Sigma x_n^4-b^4(c^8-b^8)]^4$$
$$=[bc^3(c^8-b^8-2\Sigma x_n^4)]^4+[2c^4\Sigma x_n^4+b^4(c^8-b^8)]^4$$
$$+[2bc(c^8-b^8)]^4(x_1^4+x_2^4+\ \ldots\ +x_n^4) \qquad (4)$$

Equation (4) is an algebraical solution of the equation

$$P'_1{}^4+P'_2{}^4=P_1^4+P_2^4+\ \ldots\ +P_m^4,$$

for all values of m greater than 2.

Many particular results of some interest are included in (4). Thus taking $n=2$ and putting $x_1=b^2$, $x_2=bc$, (4) becomes

$$[bc^3(c^8-b^8+2b^4\overline{b^4+c^4})]^4+[2c^4\cdot b^4(b^4+c^4)-b^4(c^8-b^8)]^4$$
$$=[bc^3(c^8-b^8-2b^4\overline{b^4+c^4})]^4+[2c^4\cdot b^4(b^4+c^4)+b^4(c^8-b^8)]^4$$
$$+[2bc(b^8-c^8)]^4(b^8+b^4c^4).$$

Hence dividing each root by (b^4+c^4) we have

$$[bc^3(b^4+c^4)]^4+[b^4(b^4+c^4)]^4=[bc^3(c^4-3b^4)]^4+[b^4(3c^4-b^4)]^4$$
$$+[2b^3c(b^4-c^4)]^4+[2b^2c^2(b^4-c^4)]^4,$$

or, as it may be written

$$b^{12}+c^{12}=\left[\frac{c^3(c^4-3b^4)}{b^4+c^4}\right]^4+\left[\frac{b^3(3c^4-b^4)}{b^4+c^4}\right]^4+\left[\frac{2b^2c(b^4-c^4)}{b^4+c^4}\right]^4+\left[\frac{2bc^2(b^4-c^4)}{b^4+c^4}\right]^4. \qquad (5)$$

The equations (4) and (5) have an important application to the solution of the problem of finding a number of biquadrates whose sum is a biquadrate.[1]

[1] See the writer's paper, Part III, Quest. 2.

(iii) We may replace x^4 in (3) by $\Sigma_{n=1}^{n=n} x_n^4 - \Sigma_{r=1}^{r=r} y_r^4$, whence we have

$$[bc^3(c^8-b^8+2\Sigma x_n^4-2\Sigma y_r^4)]^4+[2c^4(\Sigma x_n^4-\Sigma y_r^4)-b^4(c^8-b^8)]^4 +[2bc(b^8-c^8)]^4\Sigma y_r^4$$
$$=[bc^3(c^8-b^8-2\Sigma x_n^4+2\Sigma y_r^4)]^4+[2c^4(\Sigma x_n^4-\Sigma y_r^4)+b^4(c^8-b^8)]^4 +[2bc(b^8-c^8)]^4\Sigma x_n^4. \quad (6)$$

Equation (6) is an algebraical solution of the equation

$$P_1^4+P_2^4+ \ldots +P_{n+2}^4=P'_1{}^4+P'_2{}^4+ \ldots +P_{r+2}^4,$$

for all values of n and r except the case $n=r=0$.

(iv) A still more general result may be obtained by replacing in (4) and (6) Σx_n^4 by $\Sigma\lambda_n x_n^4$ and Σy_r^4 *by* $\Sigma\mu_r y_r^4$.

N.B.—There are other equations which, like (3), possess the property of indefinite extension by substitution for one of the variables. One other example will suffice, viz. :—

$$(3z^3+3z^2-3z-3+x^4)^4+(3z^3-3z^2-3z+3-x^4)^4+(6z^2-6-x^4)^4$$
$$=(3z^3+3z^2-3z-3-x^4)^4+(3z^3-3z^2-3z+3+x^4)^4+(6z^2-6+x^4)^4 +\{6x(z^2-1)\}^4. \quad (7)$$

Thus $x=1$, $z=2$ gives

$$8^4+17^4+28^4=10^4+18^4+19^4+26^4.$$

Since the quantity x only occurs in the form x^4 in (7) it is clear that we may replace it as before by $\Sigma x_n^4-\Sigma y_r^4$ and obtain an identity of the form.

$$P_1^4+P_2^4+ \ldots +P_{n+3}^4=P'_1{}^4+P'_2{}^4+ \ldots +P'_{r+4}{}^4,$$

which holds for all values of n and r, except $n=r=0$.

SECTION II—On the algebraical solution of the equation

$$\lambda Q_1^4+\mu Q_2^4=\lambda Q'_1{}^4+\mu Q'_2{}^4+\nu_1 P_1^4+\nu_2 P_2^4+ \ldots +\nu_r P_r^4$$

§ 1. As in the previous case we shall first give solutions for a few particular values of r.

QUESTION 1. Solve in integers the equation

$$\lambda P_1^4+\mu P_2^4=\lambda P'_1{}^4+\mu P'_2{}^4. \quad (1)$$

Assume as before

$$\lambda(x_1r+a)^4+\mu(x_2r+b)^4=\lambda(x_1r+c)^4+\mu(x_2r+d)^4 \quad (2)$$

where

$$\lambda a^4+\mu b^4=\lambda c^4+\mu d^4 \quad (3)$$

On expansion and rearrangement, (2) becomes

$$4(\lambda a x_1^3+\mu b x_2^3-\lambda c x_1^3-\mu d x_2^3)r^3+6(\lambda a^2 x_1^2+\mu b^2 x_2^2-\lambda c^2 x_1^2 -\mu d^2 x_2^2)r^2+4(\lambda a^3 x_1+\mu b^3 x_2-\lambda c^3 x_1-\mu d^3 x_2)r=0 \quad (4)$$

To make the coefficient of r vanish we take

$$x_1=\mu(d^3-b^3)x_2/\lambda(a^3-c^3). \quad (5)$$

Equation (4) is then identically satisfied by taking

$$r=\frac{3[\lambda(c^2-a^2)x_1^2+\mu(d^2-b^2)x_2^2]}{2[\lambda(a-c)x_1^3+\mu(b-d)x_2^3]}$$

$$=\frac{3\lambda(a^3-c^3)[\mu(c^2-a^2)(d^3-b^3)^2+\lambda(d^2-b^2)(a^3-c^3)^2]}{2x_2[\mu^2(a-c)(d^3-b^3)^3+\lambda^2(b-d)(a^3-c^3)^3]}$$

on substituting for x_1 its value given by (5).

Hence

$$x_1r+a=\frac{3\mu(d^3-b^3)[\mu(c^2-a^2)(d^3-b^3)^2+\lambda(d^2-b^2)(a^3-c^3)^2]}{2[\mu^2(a-c)(d^3-b^3)^3+\lambda^2(b-d)(a^3-c^3)^3]}+a$$

i.e. if we write Δ for $2[\mu^2(a-c)(d^3-b^3)^3+\lambda^2(b-d)(a^3-c^3)^3]$

$$\Delta(x_1r+a)=\mu^2(d^3-b^3)^2(3c^2-3a^2+2a^2-2ac)+3\lambda\mu(d^2-b^2)(d^3-b^3)(a^3-c^3)^2+2\lambda^2a(b-d)(a^3-c^3)^3$$

$$=(c-a)(3c+a)(d^3-b^3)^2\mu^2+3(d^2-b^2)(d^3-b^3)(a^3-c^3)^2\lambda\mu+2a(b-d)(a^3-c^3)^3\lambda^2.$$

Also

$$x_2r+b=\frac{3\lambda(a^3-c^3)[\mu(c^2-a^2)(d^3-b^3)^2+\lambda(d^2-b^2)(a^3-c^3)^2]}{2[\mu^2(a-c)(d^3-b^3)^3+\lambda^2(b-d)(a^3-c^3)^3]}+b$$

$$\therefore\ \Delta(x_2r+b)=\lambda^2(a^3-c^3)^3(3d^2-3b^2+2b^2-2bd)+3\lambda\mu(c^2-a^2)(a^3-c^3)(d^3-b^3)^2+2b\mu^2(a-c)(d^3-b^3)^3$$

$$=(d-b)(3d+b)(a^3-c^3)^3\lambda^2+3(c^2-a^2)(a^3-c^3)(d^3-b^3)^2\lambda\mu+2b(a-c)(d^3-b^3)^3\mu^2.$$

Also

$$x_1r+c=\frac{3\mu(d^3-b^3)[\mu(c^2-a^2)(d^3-b^3)^2+\lambda(d^2-b^2)(a^3-c^3)^2}{2[\mu^2(a-c)(d^3-b^3)^3+\lambda^2(b-d)(a^3-c^3)^3]}+c$$

$$\therefore\ \Delta(x_1r+c)=2\lambda^2c(b-d)(a^3-c^3)^3+3\lambda\mu(d^2-b^2)(d^3-b^3)(a^3-c^3)^2+\mu^2(d^3-b^3)^3[3c^2-3a^2+2ac-2c^2]$$

$$=2c(b-d)(a^3-c^3)^3\lambda^2+3(d^2-b^2)(d^3-b^3)(a^3-c^3)^2\lambda\mu+(c-a)(c+3a)(d^3-b^3)^3\mu^2.$$

Also

$$x_2r+d=\frac{3\lambda(a^3-c^3)[\mu(c^2-a^2)(d^3-b^3)^2+\lambda(d^2-b^2)(a^3-c^3)^2]}{2[\mu^2(a-c)(d^3-b^3)^3+\lambda^2(b-d)(a^3-c^3)^3]}+d$$

$$\therefore\ \Delta(x_2r+d)=\lambda^2(a^3-c^3)^3(3d^2-3b^2+2bd-2d^2)+3\lambda\mu(c^2-a^2)(a^3-c^3)(d^3-b^3)^2+2\mu^2d(a-c)(d^3-b^3)^3$$
$$=(d-b)(d+3b)(a^3-c^3)^3\lambda^2+3(c^2-a^2)(a^3-c^3)(d^3-b^3)^2\lambda\mu+2d(a-c)(d^3-b^3)^3\mu^2.$$

Hence omitting Δ and the factor $(a-c)(b-d)$ common to x_1r+a, x_2r+b, x_1r+c, x_2r+d we have that if

$$\lambda a^4+\mu b^4=\lambda c^4+\mu d^4, \qquad (3)$$

then also

$$\lambda[2a(a^2+ac+c^2)(a^3-c^3)^2\lambda^2-3(b+d)(a^2+ac+c^2)(a^3-c^3)(d^3-b^3)\lambda\mu+(3c+a)(d^2+db+b^2)(d^3-b^3)^2\mu^2]^4$$
$$+\mu[(3d+b)(a^2+ac+c^2)(a^3-c^3)^2\lambda^2-3(a+c)(d^2+db+b^2)(a^3-c^3)(d^3-b^3)\lambda\mu+2b(d^2+db+b^2)(d^3-b^3)^2\mu^2]^4$$
$$=\lambda[2c(a^2+ac+c^2)(a^3-c^3)^2\lambda^2-3(b+d)(a^2+ac+c^2)(a^3-c^3)(d^3-b^3)\lambda\mu+(c+3a)(d^2+db+b^2)(d^3-b^3)^2\mu^2]^4$$
$$+\mu[(d+3b)(a^2+ac+c^2)(a^3-c^3)^2\lambda^2-3(a+c)(d^2+db+b^2)(a^3-c^3)(d^3-b^3)\lambda\mu+2d(d^2+db+b^2)(d^3-b^3)^2\mu^2]^4,$$

that is to say, if one solution of equation (1) be known, another can be found. This second solution will not be algebraical, nor if we attempt to satisfy (3) by putting $c^2=a^2$, $d^2=b^2$ will it be anything but nugatory. If, however, any solution of (3) other than $c^2=a^2$, $d^2=b^2$ be used, a second solution, in general distinct from the first, will be found and so on *ad infinitum*.

Thus, for example, to solve the equation

$$P_1^4+3P_2^4=P'_1{}^4+3P'_2{}^4,$$

starting from the particular case $2^4+3\cdot3^4=4^4+3\cdot1^4$, we derive the following :—

a	b	c	d	$P_1^4+3P_2^4=P'_1{}^4+3P'_2{}^4$
2	−3	4	1	$23^4+3\cdot27^4 = 37^4+3\cdot1^4$
2	3	4	−1	$661^4+3\cdot147^4 = 127^4+3\cdot503^4$
2	3	4	1	$1141^4+3\cdot2589^4=3217^4+3\cdot1769^4$
−2	3	4	1	$3703^4+3\cdot5691^4=6517^4+3\cdot4753^4$

Again, putting $d=0$, we have that if $\lambda a^4+\mu b^4=\lambda c^4$, then also

$$\lambda[2a(a^2+ac+c^2)(a^3-c^3)^2\lambda^2+3b^4(a^2+ac+c^2)(a^3-c^3)\lambda\mu + (3c+a)b^8\mu^2]^4 + \mu[b(a^2+ac+c^2)(a^3-c^3)^2\lambda^2+3(c+a)b^5(a^3-c^2)\lambda\mu+2b^9\mu^2]^4 = \lambda[2c(a^2+ac+c^2)(a^3-c^3)^2\lambda^2+3b^4(a^2+ac+c^2)(a^3-c^3)b^4\lambda\mu + (c+3a)b^8\mu^2]^4 + \mu[3b(a^2+ac+c^2)(a^3-c^3)^2\lambda^2+3(c+a)(a^3-c^3)b^5\lambda\mu]^4.$$

Thus to solve $P_1^4+5P_2^4=P'_1{}^4+5P'_2{}^4$, since $1^4+5\cdot2^4=3^4+5\cdot0^4$, we derive

a	b	c	$P_1^4+5P_2^4=P'_1{}^4+5\cdot P'_2{}^4$
1	2	3	$19^4+5\cdot281^4=417^4+5\cdot117^4$
−1	2	3	$71^4+5\cdot101^4=147^4+5\cdot63^4$

§ 2. The equation $\lambda P_1^4+\mu P_2^4=\lambda P'_1{}^4+\mu P'_2{}^4+l$ is always soluble whatever be the value of l, provided a particular solution be known. For by putting $P_1=x+y$, $P_2=u-v$, $P'_1=x-y$, and $P'_2=u+v$, it becomes

$$8\lambda(x^3y+xy^3)=8\mu(u^3v+uv^3)+l$$

which is an indeterminate cubic in x and u. We proceed to solve the case where $l=\nu(P'_3{}^4-P_3^4)$.

QUESTION 2. Solve the equation

$$\lambda P_1^4+\mu P_2^4+\nu P_3^4=\lambda P'_1{}^4+\nu P'_2{}^4+\nu P'_3{}^4, \tag{1}$$

knowing a particular solution, say

$$\lambda a^4+\mu b^4+\nu c^4=\lambda d^4+\mu e^4+\nu f^4 \tag{2}$$

Here we may assume for equation (1)

$$\lambda(x_1r+a)^4+\mu(x_2r+b)^4+\nu(x_3r+c)^4=\lambda(x_1r+d)^4+\mu(x_2r+e)^4 + \nu(x_3r+f)^4 \tag{3}$$

which on expansion and rearrangement becomes

$$4(\lambda\overline{a-dx_1}^3+\mu\overline{b-ex_2}^3+\nu\overline{c-fx_3}^3)r^3+6(\lambda\overline{a^2-d^2x_1}^2+\mu\overline{b^2-e^2x_2}^2 + \nu\overline{c^2-f^2x_3}^2)r^2+4(\lambda\overline{a^3-d^3x_1}+\mu\overline{b^3-e^3x_2}+\nu\overline{c^3-f^3x_3})r=0 \tag{4}$$

To make the coefficient of r vanish we must take

$$x_3=[\lambda(a^3-d^3)x_1+\mu(b^3-e^3)x_2]/\nu(f^3-c^3) \tag{5}$$

Equation (4) is then satisfied by taking

$$r=\frac{-3[\lambda(a^2-d^2)x_1^2+\mu(b^2-e^2)x_2^2+\nu(c^2-f^2)x_3^2]}{2[\lambda(a-d)x_1^3+\mu(b-e)x_2^3+\nu(c-f)x_3^3]}$$

$$=\frac{-3\nu(f^3-c^3)[\{\lambda(a^2-d^2)x_1^2+\mu(b^2-e^2)x_2^2\}\nu(f^3-c^3)(f^2+fc+c^2)-\nu(c+f)\{\lambda(a^3-d^3)x_1+\mu(b^3-c^3)x_2\}^2]}{2[\{\lambda(a-d)x_1^3+\mu(b-e)x_2^3\}\nu^2(f^3-c^3)^2(f^2+fc+c^2)-\{\lambda(a^3-d^3)x_1+\mu(b^3-e^3)x_2\}^3]},$$

on substituting for x_3 its value given by (5). These values of x_3 and r when substituted in (3) render it an identity and constitute a solution which is clearly algebraical.

To satisfy equations (3) the solutions $d^2=a^2$, $e^2=b^2$, $f^2=c^2$ obviously make r zero and therefore lead to no new result, but we shall presently show how solutions of a different character may be obtained whatever be the values of λ, μ, and ν.

§ 3. We shall now show how the equation

$$\lambda Q_1^4+\mu Q_2^4=\lambda Q'_1{}^4+\mu Q'_2{}^4+\nu_1 P_1^4+\nu_2 P_2^4+\ \ldots\ +\nu_r P_r^4$$

may be solved by a single formula which holds for all values of r except zero.

Let us first solve the equation

$$\lambda Q_1^4+\mu Q_2^4=\lambda Q'_1{}^4+\mu Q'_2{}^4+\nu(2P)^4. \qquad (1)$$

Putting $Q_1=a+b$, $Q_2=c-d$, $Q'_1=a-b$, $Q'_2=c+d$, $P=ax$, (1) becomes

$$\lambda a^3b+\lambda ab^3=\mu c^3d+\mu cd^3+2\nu a^4x^4 \qquad (2)$$

If now we take $d=\lambda ab^3/\mu c^3$, (2) is satisfied by taking

$$\lambda a^3b=\mu\lambda^3a^3b^9/\mu^3c^8+2\nu a^4x^4$$

i.e.
$$a=\lambda b(\mu^2c^8-\lambda^2b^8)/2\mu^2\nu c^8x^4 \qquad (3)$$

so that
$$d=\lambda^2b^4(\mu^2c^8-\lambda^2b^8)/2\mu^3\nu c^{11}x^4.$$

Hence, omitting the common denominator, and replacing x throughout by x/c^2, we have as a solution of (1)

$$Q_1=\lambda\mu bc^3(\mu^2c^8-\lambda^2b^8)+2\mu^3\nu bc^3x^4,\quad Q_2=2\mu^3\nu c^4x^4-\lambda^2b^4(\mu^2c^8-\lambda^2b^8),$$
$$Q'_1=\lambda\mu bc^3(\mu^2c^8-\lambda^2b^8)-2\mu^3\nu bc^3x^4,\quad Q'_2=2\mu^3\nu c^4x^4+\lambda^2b^4(\mu^2c^8-\lambda^2b^8)$$
$$2P=2\lambda\mu bc(\mu^2c^8-\lambda^2b^8)x.$$

Thus we have the identity

$$\lambda[bc^3\{\lambda\mu(\mu^2c^8-\lambda^2b^8)+2\mu^3\nu x^4\}]^4+\mu[2\mu^3\nu c^4x^4-\lambda^2b^4(\mu^2c^8-\lambda^2b^8)]^4$$
$$=\lambda[bc^3\{\lambda\mu(\mu^2c^8-\lambda^2b^8)-2\mu^3\nu x^4\}]^4+\mu[2\mu^3\nu c^4x^4+\lambda^2b^4(\mu^2c^8-\lambda^2b^8)]^4$$
$$+\nu[2\lambda\mu bc(\mu^2c^8-\lambda^2b^8)x]^4 \qquad (4)$$

If in this we replace x^4 by x^4-y^4 we obtain

$$\lambda[bc^3\{\lambda\mu(\mu^2c^8-\lambda^2b^8)+2\mu^3\nu(x^4-y^4)\}]^4+\mu[2\mu^3\nu c^4(x^4-y^4)-\lambda^2b^4(\mu^2c^8-\lambda^2b^8)]^4+\nu[2\lambda\mu bc(\mu^2c^8-\lambda^2b^8)y]^4$$
$$=\lambda[bc^3\{\lambda\mu(\mu^2c^8-\lambda^2b^8)-2\mu^3\nu(x^4-y^4)\}]^4+\mu[2\mu^3\nu c^4(x^4-y^4)+\lambda^2b^4(\mu^2c^8-\lambda^2b^8)]^4+\nu[2\lambda\mu bc(\mu^2c^8-\lambda^2b^8)x]^4 \quad (5)$$

Equation (5) is an algebraical solution of the equation

$$\lambda P_1^{\,4}+\mu P_2^{\,4}+\nu P_3^{\,4}=\lambda P'_1{}^4+\mu P'_2{}^4+\nu P'_3{}^4$$

for all finite values of λ, μ, and ν.

Thus, putting $c=x=2$, $b=y=1$, equation (5) becomes

$$\lambda[8\{\lambda\mu(256\mu^2-\lambda^2)+30\mu^3\nu\}]^4+\mu[480\mu^3\nu-\lambda^2(256\mu^2-\lambda^2)]^4+\nu[4\lambda\mu(256\mu^2-\lambda^2)]^4$$
$$=\lambda[8\{\lambda\mu(256\mu^2-\lambda^2)-30\mu^3\nu\}]^4+\mu[480\mu^3\nu+\lambda^2(256\mu^2-\lambda^2)]^4+\nu[8\lambda\mu(256\mu^2-\lambda^2)]^4 \quad (6)$$

For example $\lambda=2$, $\mu=1$, $\nu=3$ gives

$$3^4+2\cdot33^4+3\cdot14^4=17^4+2\cdot23^4+3\cdot28^4.$$

Again, if in (4) we replace νx^4 by $\sum_{r=1}^{r=r}\nu_r x_r^{\,4}-\sum_{r=1}^{r=r}\nu_r y_r^{\,4}$, we obtain an equation

$$\lambda[bc^3\{\lambda\mu(\mu^2c^8-\lambda^2b^8)-2\mu^3(\Sigma\nu_r x_r^{\,4}-\Sigma\nu_r y_r^{\,4})\}]^4+\mu[2\mu^3c^4(\Sigma\nu_r x_r^{\,4}-\Sigma\nu_r y_r^{\,4})+\lambda^2b^4(\mu^2c^8-\lambda^2b^8)]^4+[2\lambda\mu bc(\mu^2c^8-\nu^2b^8)]^4(\nu_1x_1^{\,4}+\nu_2x_2^{\,4}+\ \ldots\ +\nu_rx_r^{\,4})$$
$$=\lambda[bc^3\{\lambda\mu(\mu^2c^8-\lambda^2b^8)+2\mu^3(\Sigma\nu_r x_r^{\,4}-\Sigma\nu_r y_r^{\,4})\}]^4+\mu[2\mu^3c^4(\Sigma\nu_r x_r^{\,4}-\Sigma\nu_r y_r^{\,4})-\lambda^2b^4(\mu^2c^8-\lambda^2b^8)]^4+[2\lambda\mu bc(\mu^2c^8-\nu^2b^8)]^4(\nu_1y_1^{\,4}+\nu_2y_2^{\,4}+\ \ldots\ +\nu_ry_r^{\,4}) \quad (7)$$

which is an algebraical solution of the equation

$$\lambda_1P_1^{\,4}+\lambda_2P_2^{\,4}+\ \ldots\ +\lambda_{r+2}P_{r+2}^{4}=\lambda_1P'_1{}^4+\lambda_2P'_2{}^4+\ \ldots\ +\lambda_{r+2}P'^{\,4}_{r+2}$$

for all values of r except $r=0$.

Finally, if in (7) we put all the y's equal to zero, we obtain

$$\lambda[bc^3\{\lambda\mu(\mu^2c^8-\lambda^2b^8)+2\mu^3\Sigma\nu_r x_r^{\,4}\}]^4+\mu[2\mu^3c^4\Sigma\nu_r x_r^{\,4}-\lambda^2b^4(\mu^2c^8-\lambda^2b^8)]^4$$
$$=\lambda[bc^3\{\lambda\mu(\mu^2c^8-\lambda^2b^8)-2\mu^3\Sigma\nu_r x_r^{\,4}\}]^4+\mu[2\mu^3c^4\Sigma\nu_r x_r^{\,4}+\lambda^2b^4(\mu^2c^8-\lambda^2b^8)]^4+[2\lambda\mu bc(\mu^2c^8-\nu^2b^8)]^4(\nu_1x_1^{\,4}+\nu_2x_2^{\,4}+\ \ldots\ +\nu_rx_r^{\,4}) \quad (8)$$

which is an algebraical solution of the equation

$$\lambda Q_1^4+\mu Q_2^4=\lambda Q'_1{}^4+\mu Q'_2{}^4+\nu_1 P_1^4+\nu_2 P_2^4+ \ . \ . \ . \ +\nu_r P_r^4,$$

where λ, μ, ν_1, ν_2, ν_3, . . ., ν_r are arbitrary coefficients, positive or negative, which are unrestricted except that λ and μ are both finite, and the ν's do not all vanish—a result of considerable generality.

Part III

§ 1. The equation

$$P_0^4=P_1^4+P_2^4+\ldots+P_n^4$$

has been shown by Euler [1] to be insoluble when $n=2$, and there is reason to believe that it is also insoluble when $n=3$, although no demonstration has ever been given.[2] The case $n=4$ does not appear to have been solved either algebraically or otherwise, but the present writer has discovered one numerical solution, which shows that the equation is soluble. When n exceeds 4 there is no great difficulty in obtaining algebraical solutions, but these are of a very specialised character, on account of the particular assumptions made as to the forms of the roots, and are not at all to be regarded as typical of the general rule.

It will be convenient to commence with the cases $n=5$, 6, and 7 (§§ 2-4) from the formulæ for which it will be shown algebraical solutions for all values of n greater than 7 may be deduced, then to proceed in the light of these results to discuss the case $n=4$ (§ 6), and finally to give algebraical solutions for all values of n greater than 2 of the equation transformed by replacing P_0^4 by P_0^2 (§ 7).

§ 2. Question 1. Solve the equation

$$P_0^4=P_1^4+P_2^4+P_3^4+P_4^4+P_5^4.$$

We have identically

$$(u^2+v^2)^4=(u^2-v^2)^4+(2uv)^4+2[2uv(u^2-v^2)]^2$$

and

$$(x+y)^4+(x-y)^4+(2y)^4=2(x^2+3y^2)^2.$$

[1] *Elements of Algebra*, Fourth Edition, 1828, Part II., Chap. xiii. §§ 206-208.

[2] Cf. Euler, *Commentationes Arithmeticæ*, vol. I., xxxiii. § 1; vol. II., lxviii. § 3.

Hence we shall have

$$(u^2+v^2)^4=(u^2-v^2)^4+(2uv)^4+(x+y)^4+(x-y)^4+(2y)^4 \quad (1)$$

provided $$2uv(u^2-v^2)=x^2+3y^2 \quad (2)$$

Now if for the moment we regard v as a constant, equal to v' say, this equation may be written

$$2uv'(u^2-v'^2)=x^2+3y^2,$$

which, being a non-homogeneous indeterminate cubic in u, x, y, can be solved algebraically, if a particular solution is known.[1] But a particular solution of it is obviously $u=2$, $v'=1$, $x=3$, $y=1$, and others are easily found, for example, $(u, v, x, y)=(7, 6, 3, 19)$, or $(7, 6, 15, 17)$, or $(7, 6, 27, 11)$, or $(7, 6, 33, 1)$. Hence an algebraical solution may be found.

To solve (2) we may therefore put

$$u=x_1r+u',\ v=v',\ x=x_2r+x',\ y=x_3r+y' \quad (3)$$

where we suppose (u', v', x', y') to be a particular solution of (2), *i.e.*

$$2u'v'(u'^2-v'^2)=x'^2+3y'^2 \quad (4)$$

Making the substitutions (3), equation (2) then becomes

$$2(x_1r+u')v'[(x_1r+u')^2-v'^2]=(x_2r+x')^2+3(x_3r+y')^2$$

or, on expansion and rearrangement according to powers of r, in virtue of (4),

$$(2v'x_1^3)r^3+(6u'v'x_1^2-x_2^2-3x_3^2)r^2+2[x_1v'(u'^2-v'^2)+2u'^2v'x_1-x_2x'-3x_3y']r=0 \quad (5)$$

To make the coefficient of r vanish we must have

$$(3u'^2v'-v'^3)x_1-x_2x'-3x_3y'=0$$

say, $$x_3=\{(3u'^2v'-v'^3)x_1-x'x_2\}/3y' \quad (6)$$

Equation (5) is now satisfied by taking

$$\begin{aligned} r&=(x_2^2+3x_3^2-6u'v'x_1^2)/2v'x_1^3 \\ &=\frac{3y'^2x_2^2+(3u'^2v'-v'^3)^2x_1^2-2x'(3u'^2v'-v'^3)x_1x_2+x'^2x_2^2-18u'v'y'^2x_1^2}{6v'y'^2x_1^3} \\ &=\frac{[v'(3u'^2-v'^2)^2-18u'y'^2]x_1^2-2x'(3u'^2-v'^2)x_1x_2+2u'(u'^2-v'^2)x_2^2}{6y'^2x_1^3} \end{aligned} \quad (7)$$

on substituting the value of x_3 given by (6).

[1] See the writer's paper, Part I.

Hence we have

$$u=x_1r+u'=\frac{[v'(3u'^2-v'^2)^2-12u'y'^2]x_1^2-2x'(3u'^2-v'^2)x_1x_2+2u'(u'^2-v'^2)x_2^2}{6y'^2x_1^2}$$

$$x=x_2r+x'=\frac{6x'y'^2x_1^3+[v'(3u'^2-v'^2)^2-18u'y'^2]x_1^2x_2-2x'(3u'^2-v'^2)x_1x_2^2+2u'(u'^2-v'^2)x_2^3}{6y'^2x_1^3}$$

$$y=x_3r+y'=\frac{[\{u'(3u'^2-v'^2)^2-18u'y'^2\}x_1^2-2x'(3u'^2-v'^2)x_1x_2+2u'(u'^2-v'^2)x_2^2][(3u'^2v'-v'^3)x_1-x'x_2]}{18y'^3x_1^3}+y'$$

$$\begin{aligned}=[&[(3u'^2v'-v'^3)\{v'(3u'^2-v'^2)^2-18u'y'^2\}+18y'^4]x_1^3\\&-[x'\{v'(3u'^2-v'^2)^2-18u'y'^2\}+2x'v'(3u'^2-v'^2)^2]x_1^2x_2\\&+(3u'^2-v'^2)\{2u'v'(u'^2-v'^2)+2x'^2\}x_1x_2^2-2u'x'(u'^2-v'^2)x_2^3]\\&/18y'^3x_1^3.\end{aligned}$$

In these equations u', v', x', y' must have such values as satisfy equation (4). Thus if we take $u'=2$, $v'=1$, $x'=3$, $y'=1$, we shall have

$$\begin{aligned}u&=(97x_1^2-66x_1x_2+12x_2^2)/6x_1^2, \qquad v=1,\\x&=(18x_1^3+85x_1^2x_2-66x_1x_2^2+12x_2^3)/6x_1^3,\\y&=(953x_1^3-981x_1^2x_2+330x_1x_2^2-36x_2^3)/18x_1^3.\end{aligned}$$

These give, finally, the identity

$$\begin{aligned}[(97x_1^2-66x_1x_2+12x_2^2)^2+(6x_1^2)^2]^4=&[(97x_1^2-66xy+12x_2^2)^2\\&-(6x_1^2)^2]^4\\&+[12x_1^2(97x_1^2-66x_1x_2+12x_2^2)]^4+[4x_1(953x_1^3-981x_1^2x_2\\&+330x_1x_2^2-36x_2^3)]^4\\&+[2x_1(1007x_1^3-726x_1^2x_2+132x_1x_2^2)]^4+[2x_1(899x_1^3-1236x_1^2x_2\\&+528x_1x_2^2-72x_2^3)]^4 \qquad (8)\end{aligned}$$

The solution $u=2$, $v=1$, $x=3$, $y=1$ gives from (1)

$$5^4=3^4+4^4+4^4+2^4+2^4$$

and $u=7$, $v=6$, $x=3$, $y=19$ gives

$$85^4=84^4+38^4+22^4+16^4+13^4.$$

If in (8) we put $x_1=1$, $x_2=2$, we derive

$$205^4=166^4+156^4+133^4+92^4+74^4.$$

It is to be remarked that if we have any solution of the form

$$\begin{aligned}P_0^4&=P_1^4+P_2^4+(x+y)^4+(x-y)^4+(2y)^4\\&=P_1^4+P_2^4+2(x^2+3y^2)^2\end{aligned}$$

we may derive others from it of the same form by multiplying by $(p^2+3q^2)^4$. For we then have

$$\{P_0(p^2+3q^2)\}^4=\{P_1(p^2+3q^2)\}^4+\{P_2(p^2+3q^2)\}^4+2(x^2+3y^2)^2(p^2+3q^2)^4 \quad (9)$$

But $2(x^2+3y^2)^2(p^2+3q^2)^4$ is expressible in the form $2(A^2+3B^2)^2$, where

$$A=(p^2-3q^2)x+6pqy,\ B=2pqx-(p^2-3q^2)y,$$

(A and B having in general a variety of values depending on the composite character of x^2+3y^2 and of p^2+3q^2).

Hence (9) becomes

$$\{P_0(p^2+3q^2)\}^4=\{P_1(p^2+3q^2)\}^4+\{P_2(p^2+3q^2)\}^4+2(A^2+3B^2)^2$$
$$=\{P_1(p^2+3q^2)\}^4+\{P_2(p^2+3q^2)\}^4+(A+B)^4+(A-B)^4+(2B)^4$$

and since p and q are arbitrary this will give an infinity of solutions.

In practice, where an arithmetical result merely is desired, we proceed as follows. Starting from any solution of the required form, say

$$5^4=4^4+3^4+4^4+2^4+2^4$$
$$=4^4+3^4+2\cdot 12^2.$$

we multiply this by 7^4 say, 7 being the smallest integer of the form p^2+3q^2, and obtain

$$35^4=28^4+21^4+2\cdot 12^2(1^2+3\cdot 4^2)^2$$
$$=28^4+21^4+2(24^2+3\cdot 2^2)^2$$
$$=28^4+21^4+26^4+22^4+4^4.$$

A second application of this process gives

$$245^4=196^4+188^4+147^4+142^4+46^4.$$

Similar results may be obtained by multiplying by 13^4, 19^4, etc.

The defect of all the foregoing solutions lies manifestly in the assumption that $P_3+P_4=P_5$, a restriction which such identities as

$$31^4=30^4+17^4+10^4+10^4+10^4,$$
$$313^4=312^4+90^4+75^4+70^4+30^4,$$

etc., show to be unnecessary.

§ 3. QUESTION 2. Solve the equation

$$P_0^4=P_1^4+P_2^4+P_3^4+P_4^4+P_5^4+P_6^4. \qquad (1)$$

In a former paper [1] there occurs the identity

$$[bc^3(c^8-b^8+2\Sigma x_n^4)]^4+[2c^4\Sigma x_n^4-b^4(c^8-b^8)]^4$$
$$=[bc^3(c^8-b^8-2\Sigma x_n^4)]^4+[2c^4\Sigma x_n^4+b^4(c^8-b^8)]^4+[2bc(c^8-b^8)]^4$$
$$(x_1^4+x_2^4+\ \ldots\ +x_n^4).$$

From this we see that if

$$b^8-c^8=2\Sigma x_n^4 \qquad (2)$$

then $[2c^4\Sigma x_n^4-b^4(c^8-b^8)]^4=[bc^3(c^8-b^8-2\Sigma x_n^4)]^4+$
$[2c^4\Sigma x_n^4+b^4(c^8-b^8)]^4+[2bc(b^8-c^8)]^4(x_1^4+x_2^4+\ \ldots\ .\ +x_n^4)$
i.e. on making use of (2) and dividing each root by c^8-b^8,

$$(b^4+c^4)^4=(b^4-c^4)^4+(2bc^3)^4+(2bc)^4(x_1^4+x_2^4+\ \ldots\ +x_n^4) \qquad (3)$$

a result which is immediately obvious from the fact that we have identically

$$(b^4+c^4)^4=(b^4-c^4)^4+8b^4c^4(b^8+c^8)$$
$$=(b^4-c^4)^4+(2bc^3)^4+8b^4c^4(b^8-c^8).$$

Now the equation (2) is soluble algebraically when n is of the form 2^{r+2}. For, if in the identity

$$(x+y)^4-(x-y)^4=8xy(x^2+y^2),$$

we replace x by x^4 and y by $4y^4$ we derive

$$(x^4+4y^4)^4-(x^4-4y^4)^4=2(2xy)^4(x^8+16y^8),$$

so that multiplying each side by $(x^4+4y^4)^4+(x^4-4y^4)^4$ we have

$$(x^4+4y^4)^8-(x^4-4y^4)^8=2(2xy)^4(x^8+16y^8)](x^4+4y^4)^4$$
$$+(x^4-4y^4)^4] \qquad (4)$$

Hence as a solution of equation (1) we have, putting $b=x^4+4y^4$, $c=x^4-4y^4$ in (3)

$P_0=(x^4+4y^4)^4+(x^4-4y^4)^4$, $\quad P_1=(x^4+4y^4)^4-(x^4-4y^4)^4$,
$P_2=2(x^4+4y^4)(x^4-4y^4)^3$, $\quad P_3=4x^3y(x^4+4y^4)^2(x^4-4y^4)$,
$P_4=4x^3y(x^4+4y^4)(x^4-4y^4)^2$, $\quad P_5=8xy^3(x^4+4y^4)^2(x^4-4y^4)$,
$P_6=8xy^3(x^4+4y^4)(x^4-4y^4)^2$.

[1] Viz., Part II.

Thus we have the identity

$$[(x^4+4y^4)^4+(x^4-4y^4)]^4=[(x^4+4y^4)^4-(x^4-4y^4)]^4+[2(x^4+4y^4)(x^4-4y^4)^3]^4$$
$$+[4x^3y(x^4+4y^4)^2(x^4-4y^4)]^4+[4x^3y(x^4+4y^4)(x^4-4y^4)^2]^4$$
$$+[8xy^3(x^4+4y^4)^2(x^4-4y^4)]^4+(8xy^3(x^4+4y^4)(x^4-4y^4)^2]^4. \quad (5)$$

For example, $x=y=1$ gives, on omission of the common factor 2,

$$353^4=272^4+135^4+300^4+150^4+180^4+90^4.$$

Again, if for shortness we put X for x^4+4y^4 and Y for x^4-4y^4, then equation (4) is

$$X^8-Y^8=2(2xy)^4(x^8+16y^8)(X^4+Y^4).$$

Multiplying each side of this equation by X^8+Y^8 it becomes

$$X^{16}-Y^{16}=2(2xy)^4(x^8+16y^8)(X^4+Y^4)(X^8+Y^8),$$

and if we multiply each side of this again by $X^{16}+Y^{16}$, it becomes

$$X^{32}-Y^{32}=2(2xy)^4(x^8+16y^8)(X^4+Y^4)(X^8+Y^8)(X^{16}+Y^{16}),$$

and in general we have

$$X^{2r+3}-Y^{2r+3}=2(2xy)^4(x^8+16y^8)(X^4+Y^4)(X^8+Y^8)\ \ldots$$
$$(X^{2r+2}+Y^{2r+2}) \quad (6)$$

Now the right-hand side of (6), omitting the factor $2\,(2xy)^4$, consists of the product of $^{r+2}$ factors each of which is the sum of two biquadrates, and therefore the right-hand side of (6) is equal to twice the sum of 2^{r+2} biquadrates, which we may call $x_1, x_2, x_3, \ldots, x_{2r+2}$. Hence $b=X^{2r}$, $c=Y^{2r}$ is an algebraic solution of (2), for the case $n=2^{r+2}+2$, giving, on substitution in (3), the identity

$$[X^{2r+2}+Y^{2r+2}]^4=[X^{2r+2}-Y^{2r+2}]^4+]2X^{2r}Y^{3\cdot 2r}]^4$$
$$+[4xyX^{2r}Y^{2r}]^4(x^8+16y^8)(X^4+Y^4)(X^8+Y^8)\ \ldots\ (X^{2r+2}+Y^{2r+2})$$

Thus $r=1$ gives

$$[X^8+Y^8]^4=[X^8-Y^8]^4+[2X^2Y^6]^4+[4xyX^4Y^4]^4(x^8+16y^8)(X^4+Y^4)(X^8+Y^8),$$

which is an algebraical solution of

$$P_0^4=P_1^4+P_2^4+\ \ldots\ +P_{10}^4.$$

Cor. We may now give algebraical solutions of the equation

$$P_0^4=P_1^4+P_2^4+\ \ldots\ +P_r^4,$$

where $r=6+2m$.

For we have the identity [1]

$$b^{12}+c^{12}=\frac{[b^3(b^4-3c^4)]^4+[c^3(c^4-3b^4)]^4+[2b^2c(b^4-c^4)]^4+[2bc^2(b^4-c^4)]^4}{(b^4+c^4)^4}$$

$$=\frac{[b^3(b^4-3c^4)]^4+[c^3(c^4-3b^4)]^4+[2bc(b^4-c^4)]^4(b^4+c^4)}{(b^4+c^4)^4}$$

Put now $b=u_1^2$, $c=2v_1^2$ and this becomes

$$u_1^{24}+2^{12}v_1^{24}=\{[u_1^6(u_1^8-48v_1^8)]^4+[8v_1^6(16v_1^8-3u_1^8)]^4 +[4u_1^4v_1^2(u_1^8-16v_1^8)]^4 +[8u_1^2v_1^4(u_1^8-16v_1^8)]^4\}/(u_1^8+16v_1^8)^4 \qquad (7)$$

Again, equation (5) is

$$[X^4+Y^4]^4=[X^4-Y^4]^4+[2XY^3]^4+[4xyX^2Y]^4(x^8+16y^8) +[4xyXY^2]^4(x^8+16y^8) \qquad (8)$$

If then we put $x=u_1^3$, $y=2v_1^3$, x^8+16y^8 becomes $u_1^{24}+2^{12}v_1^{24}$ which is expressible rationally as the sum of four biquadrates. Making these substitutions in (8) we see that if X' and Y' denote the new values of X and Y, then $[X'^4+Y'^4]^4$ is expressible simultaneously as the sum of 6, 8, or of 10 rational biquadrates which may all be made integral by multiplying each root by $(u_1^8+16v_1^8)$. As a matter of fact we have

$$[(u_1^{12}+64v_1^{12})^4+(u_1^{12}-64v_1^{12})^4]^4=[(u_1^{12}+64v_1^{12})^4 -(u_1^{12}-64v_1^{12})^4]^4 +[2(u_1^{12}+64v_1^{12})(u_1^{12}-64v_1^{12})^3]^4+[8u_1^3v_1^3(u_1^{12}+64v_1^{12}) (u_1^{12}-64v_1^{12})^2]^4[u_1^{24}+2^{12}v_1^{24}] +[8u^3{}_1v_1^3(u_1^{12}+64v_1^{12})^2(u_1^{12}-64v_1^{12})]^4[u_1^{24}+2^{12}v_1^{24}]$$

$$=[(u_1^{12}+64v_1^{12})^4-(u_1^{12}-64v_1^{12})^4]^4 +[2(u_1^{12}+64v_1^{12})(u_1^{12}-64v_1^{12})^3]^4 +[8u_1^3v_1^3(u_1^{12}+64v_1^{12})(u_1^{12}-64v_1^{12})^2]^4\{[u_1^6(u_1^8-48v_1^8)\}^4 +\{8v_1^6(16v_1^8-3u_1^8)\}^4$$

[1] See § 3 of Part I.

$$+\{4u_1^4v_1^2(u_1^8-16v_1^8)\}^4+\{8u_1^2v_1^4(u_1^8-16v_1^8)\}^4]/(u_1^8+16v_1^8)^4$$
$$+[8u_1^3v_1^3(u_1^{12}+64v_1^{12})^2(u_1^{12}-64v_1^{12})]^4[u_1^{24}+2^{12}v_1^{24}]$$
$$=[(u_1^{12}+64v_1^{12})^4-(u_1^{12}-64v_1^{12})^4]^4+[2(u_1^{12}+64v_1^{12})$$
$$(u_1^{12}-64v_1^{12})^3]^4$$
$$+[8u_1^3v_1^3(u_1^{12}+64v_1^{12})(u_1^{12}-64v_1^{12})^2]^4[\{u_1^6(u_1^8-48v_1^8)\}^4$$
$$+\{8v_1^6(16v_1^8-3u_1^8)\}^4$$
$$+\{4u_1^4v_1^2(u_1^8-16v_1^8)\}^4+\{8u_1^2v_1^4(u_1^8-16v_1^8)\}^4]/(u_1^8+16v_1^8)^4$$
$$+[8u_1^3v_1^3(u_1^{12}+64v_1^{12})^2(u_1^{12}-64v_1^{12})]^4[\{u_1^6(u_1^8-48v_1^8)\}^4$$
$$+\{8v_1^6(16v_1^8-3u_1^8)\}^4$$
$$+\{4u_1^4v_1^2(u_1^8-16v_1^8)\}^4+\{8u_1^2v_1^4(u_1^8-16v_1^8)\}^4]/(u_1^8+16v_1^8)^4.$$

Again, since on the right-hand side of (7), and therefore also on the right-hand side of (8) in its new form, the sum of two of the biquadrates is $u_1^8+16v_1^8$ multiplied by a certain factor, it follows that the substitution $u_1=u_2^3$, $v_1=2v_2^3$ will convert $u_1^8+16v_1^8$ into $u_2^{24}+2^{12}v_2^{24}$, which by (7) is expressible as the sum of four rational biquadrates (so that $u_2^{72}+2^{12}(2v_2^3)^{24}$ is expressible as the sum of four or of six biquadrates), and since as before the sum of two of these four biquadrates will be $u_2^8+16v_2^8$, multiplied by a factor, it is clear that the successive substitutions $u_2=u_3^3$, $v_2=2v_3^3$, and in general $u_r=u_{r+1}^3$, $v_r=2v_{r+1}^3$ will enable the right-hand side of (8) to be expressed simultaneously as sums of biquadrates successively increasing by 2, *i.e.* we shall have a biquadrate equal to the sum of any even number of biquadrates greater than four.

There is no great difficulty in writing down, in accordance with the above formulæ, a biquadrate equal to the sum of $6+2n$ biquadrates, but such formulæ will only give arithmetical results of a high order of magnitude, the reason being that they do not give a biquadrate merely equal to the sum of $6+2n$ biquadrates, but furnish a special kind of biquadrate which possesses the peculiar additional property of being expressible simultaneously as the sum of every even number of biquadrates greater than four up to $6+2n$.

§ 4. QUESTION 3. Solve the equation

$$P_0^4=P_1^4+P_2^4+P_3^4+P_4^4+P_5^4+P_6^4+P_7^4 \qquad (1)$$

In the identity

$$(t+1)^4=(t-1)^4+8t+8t^3$$

put $t=(x^4+y^4+z^4)/8$ and we obtain

$$\left(\frac{x^4+y^4+z^4+8}{8}\right)^4=\left(\frac{x^4+y^4+z^4-8}{8}\right)^4+x^4+y^4+z^4+\frac{(x^4+y^4+z^4)^3}{64} \qquad (2)$$

Let us now choose x, y, and z so that

$$x^4+y^4+z^4=2v^4.$$

To do this, since we have identically

$$x^4+y^4+(x+y)^4=2(x^2+xy+y^2)^2$$

it will be sufficient to take

$$x=2ab+b^2,\ y=a^2-b^2,\ z=a^2+2ab,$$

for since this makes $x^2+xy+y^2=(a^2+ab+b^2)^2$, we shall have [1]

$$(2ab+b^2)^4+(a^2-b^2)^4+(a^2+2ab)^4=2(a^2+ab+b^2)^4.$$

Making these substitutions (2) becomes

$$\left[\frac{(a^2+ab+b^2)^4+4}{4}\right]^4=\left[\frac{(a^2+ab+b^2)^4-4}{4}\right]^4+(2ab+b^2)^4+(a^2-b^2)^4$$
$$+(a^2+2ab)^4+2(a^2+ab+b^2)^{12}/16. \qquad (3)$$

Now since $2=\dfrac{(c^2-d^2)^4+(2cd+d^2)^4+(2cd+c^2)^4}{(c^2+cd+d^2)^4}$

(3) may be written

$$[(a^2+ab+b^2)^4+4]^4=[(a^2+ab+b^2)^4-4]^4+(8ab+4b^2)^4+(4a^2-4b^2)^4$$
$$+(4a^2+8ab)^4+2^4(a^2+ab+b^2)^{12}.\frac{(c^2-d^2)^4+(2cd+d^2)^4+(2cd+c^2)^4}{(c^2+cd+d^2)^4}.$$

This is an algebraical solution of equation (1) and it may be integralised by multiplying each root by (c^2+cd+d^2), or

[1] This solution of the equation $2P_0^4=P_1^4+P_2^4+P_3^4$ involves the assumption $P_1=P_2+P_3$, a restriction which the identity

$$2\cdot484813^4=575528^4+155873^4+116745^4$$

shows to be unnecessary.

simply by taking as a particular case $c=a$, $d=b$, in which case it becomes

$$[(a^2+ab+b^2)^4+4]^4=[(a^2+ab+b^2)^4-4]^4+(8ab+4b^2)^4+(4a^2-4b^2)^4 +(4a^2+8ab)^4+2^4(a^2+ab+b^2)^8[(a^2-b^2)^4+(2ab+b^2)^4+(2ab+a^2)^4].$$

For example $a=2$, $b=1$ gives

$$2405^4=2397^4+784^4+490^4+294^4+32^4+20^4+12^4.$$

Another solution, closely allied but giving smaller results, may be obtained thus. We have identically

$$(a^2+4b^2)^4=(a^2-4b^2)^4+2\cdot 2^4a^2b^2(a^4+16b^4). \qquad (4)$$

Now put $b=z^2$, $a=x^2+3y^2$, and this becomes

$$[(x^2+3y^2)^2+4z^4]^4=[(x^2+3y^2)^2-4z^4]^4+(2z)^4[(x^2+3y^2)^4+(2z^2)^4]\times [(x+y)^4+(x-y)^4+(2y)^4] \qquad (5)$$

For example, we have when

$x=y=z$, $\quad 5^4=4^4+4^4+3^4+2^4+2^4$,

$x=0$, $y=z$, $\quad 13^4=12^4+8^4+6^4+6^4+5^4+4^4+4^4$,

$x=3$, $y=z=1$, $\quad 37^4=35^4+24^4+12^4+12^4+4^4+2^4+2^4$,

$x=2$, $y=z=1$, $\quad 53^4=45^4+42^4+28^4+14^4+12^4+8^4+4^4$.

Also, since the equation

$$2Q_0{}^2=Q_1{}^4+Q_2{}^4+\ \ldots\ +Q_r{}^4$$

can be solved algebraically for all values of r greater than 2 (see § 7 *infra*), it follows that by putting $b=z^2$, $a=Q_0$ in (4) that we can get algebraical solutions of the equation

$$P_0{}^4=P_1{}^4+P_2{}^4+\ \ldots\ +P_s{}^4,$$

where $s=7+2n$.

Again, write equation (5) in the form

$$[(x^2+3y^2)^2+4z^4]^4=[(x^2+3y^2)^2-4z^4]^4+(4yz)^4[(x^2+3y^2)^4+(2z^2)^4] +(2z)^4(x^2+3y^2)^4[(x+y)^4+(x-y)^4]+(4z^3)^4[(x+y)^4+(x-y)^4] \qquad (6)$$

Now, an algebraical solution of the equation

$$Q_1{}^4+Q_2{}^4=P_1{}^4+P_2{}^4+\ \ldots\ +P_r{}^4 \qquad (7)$$

has been found [1] for all values of r greater than 2 by means of a single formula. If then, we choose x and y so that

$$x+y=Q_1,\ x-y=Q_2,$$

we can, on replacing $(x+y)^4+(x-y)^4$ by $P_1{}^4+P_2{}^4+\ \ldots\ +P_r{}^4$,

[1] See § 3 of Part II., Section 1.

in one only of the two places in which it occurs on the right-hand side of (6), say the second, write equation (6) as

$$[(x^2+3y^2)^2+4z^4]^4=[(x^2+3y^2)^2-4z^4]^4+(4yz)^4[(x^2+3y^2)^4+(2z^2)^4]$$
$$+(2z)^4(x^2+3y^2)^4(Q_1^4+Q_2^4)+(4z^3)^4(P_1^4+P_2^4+\ \ldots\ +P_r^4).$$

This is therefore an algebraical solution, by means of a single formula, of the equation

$$P_0^4=P_1^4+P_2^4+\ \ldots\ +P_s^4,$$

for all values of s greater than 6.

As before, the defect of all these solutions is the unnecessary peculiarity possessed by one (or more) of the roots of the biquadrates on the right-hand side of the equation, viz., that it is always equal to the sum of the roots of two of the remaining biquadrates.

§ 5. From the foregoing results other solutions may be obtained for various values of n. For if we have solved, arithmetically or algebraically, the equations

$$P_0^4=P_1^4+P_2^4+\ \ldots\ +P_r^4,$$
$$Q_0^4=Q_1^4+Q_2^4+\ \ldots\ Q_s^4,$$

then each of the biquadrates on the right-hand side of the equation

$$(P_0Q_0)^4=(P_1Q_0)^4+(P_2Q_0)^4+\ \ldots\ +(P_rQ_0)^4$$

may be expressed as the sum of s biquadrates so that this equation gives a biquadrate equal to the sum of $r+k(s-1)$ biquadrates, where $k=0, 1, 2, 3, \ldots, r$. This is obvious and calls for no special exemplification.

Also, for particular values of n, other independent formulæ may be found.

For example, let $n=16$. Then since

$$(2u+v)^4+(u+2v)^4+(u-v)^4=18(u^2+uv+v^2)^2,$$

we have, on putting $u=2xy+y^2$, $v=x^2-y^2$,

$$(x^2+4xy+y^2)^4+(2x^2+2xy-y^2)^4+(x^2-2xy-2y^2)^4$$
$$=18(x^2+xy+y^2)^4,$$

so that $(x^2+4xy+y^2)^4+(2x^2+2xy-y^2)^4+(x^2-2xy-2y^2)^4$
$$-\{2(x^2+xy+y^2)\}^4$$
$$=2(x^2+xy+y^2)^4.$$

Now we have identically

$$(a^4+b^4+c^4+d^4)^4-(a^4+b^4+c^4-d^4)^4=8d^4(a^4+b^4+c^4)[(a^4+b^4+c^4)^2+d^8]$$
$$=(2d^3)^4(a^4+b^4+c^4)+8d^4(a^4+b^4+c^4)[(a^4+b^4+c^4)^2-d^8]$$
$$=(2d^3)^4(a^4+b^4+c^4)+8d^4(a^4+b^4+c^4)(a^4+b^4+c^4+d^4)(a^4+b^4+c^4-d^4). \quad (1)$$

Hence if we put

$$a=x^2+4xy+y^2,\ b=2x^2+2xy-y^2,\ c=x^2-2xy-2y^2,\ d=2(x^2+xy+y^2)$$

equation (1) will become

$$(a^4+b^4+c^4+d^4)^4=(a^4+b^4+c^4-d^4)^4+(2d^3)^4(a^4+b^4+c^4)+(2d)^4(a^4+b^4+c^4)(a^4+b^4+c^4+d^4)(x^2+xy+y^2)^4,$$

which gives a biquadrate equal to the sum of 16 biquadrates.

Again, since we have identically

$$(x^2+4y^4/x^2)^2+(3y^2)^2=x^4+(2y)^4+(y)^4+(2y^2/x)^4$$

and $$(x^2+4y^4/x^2)^2-(3y^2)^2=x^4+(2y^2/x)^4-y^4$$

we have on multiplying corresponding sides of these equations together

$$(x^2+4y^4/x^2)^4-(3y^2)^4=\{x^4+(2y)^4+y^4+(2y^2/x)^4\}\{(2y^2/x)^4+x^4-y^4\}. \quad (2)$$

Hence if we can express x^4-y^4 as the sum of r biquadrates, then equation (2) will give a biquadrate equal to the sum of $1+4(r+1)$ biquadrates. Thus for example if

$$x=(a^4+4b^4)^4+(a^4-4b^4)^4,\ y=(a^4+4b^4)^4-(a^4-4b^4)^4,$$

then by § 3, Question 2, x^4-y^4 will be equal to the sum of 5 biquadrates, so that equation (2) will give a biquadrate equal to the sum of 25 biquadrates.

These examples of the extension of the results of §§ 2-4 must suffice, for, with the increase in the magnitude of n, diminishes, naturally, the difficulty of solving the equation.

§ 6. We come now to the case $n=4$, *i.e.* to the equation

$$P_0^4=P_1^4+P_2^4+P_3^4+P_4^4. \quad (1)$$

As the assumption that P_0 and P_1 are respectively the

sum and the difference of two squares has led to solutions in all cases where n is greater than 4, it is natural to try this assumption here. Now if

$$P_0=u^2+v^2,\ P_1=u^2-v^2,$$

then $$P_0^4-P_1^4=(u^2+v^2)^4-(u^2-v^2)^4=8u^2v^2(u^4+v^4). \qquad (2)$$

Now every biquadrate is of the form $5n$ or $5n+1$; hence three of the roots on the right-hand side of (1) are multiples of 5 always. If we assume that P_1 is the root prime to 5, then from (2) $8u^2v^2(u^4+v^4)$ must be divisible by 5^4. But this is impossible so long as u and v are both prime to 5. Hence, since P_0 and P_1 are both prime to 5, one of u, v is a multiple of 5 and the other prime to 5, and u^2v^2 must therefore be divisible by 5^4. Since u^2v^2 is always to be divisible by 5^4, this suggests that possibly u and v are both squares, the one always divisible by 5, and the other always prime to 5. This again suggests as a suitable transformation $u=(x^2+y^2)^2$, $v=(x^2-y^2)^2$, or on analogy with the results of Question 2, $u=(x^4+4y^4)^2$, $v=(x^4-4y^4)^2$, each of which manifestly satisfies the required condition so long as x and y are both prime to 5. Hence we are led to the assumptions

$$P_0=(x^2+y^2)^4+(x^2-y^2)^4,\ P_1=(x^2+y^2)^4-(x^2-y^2)^4 \qquad (3)$$

or $$P_0=(x^4+4y^4)^4+(x^4-4y^4)^4,\ P_1=(x^4+4y^4)^4-(x^4-4y^4)^4 \qquad (4)$$

of which the latter is merely the specialised form obtained from the former by writing in it x^2 instead of x and $2y^2$ instead of y.

It now remains to choose P_2, P_3, P_4 in such a way as to make $P_2^4+P_3^4+P_4^4$ a homogeneous symmetrical function of x and y of the 32nd or 64th degree according as we take assumption (3) or (4). This we may do in a variety of ways, but probably the simplest forms which present themselves would be

$$\left.\begin{aligned} P_2&=2(x^4-y^4)[2xy(x^2+y^2)],\\ P_3&=2(x^4-y^4)[2xy(x^2-y^2)],\\ P_4&=2(x^4-y^4)[x^4-y^4], \end{aligned}\right\} \text{ or } \left.\begin{aligned} P_2&=2(x^4-y^4)(x^4+x^2y^2+y^4)\\ P_3&=2(x^4-y^4)(xy^3)\\ P_4&=2(x^4-y^4)(x^3y), \end{aligned}\right\}$$

and the forms obtained by replacing x by x^2 and y by $2y^2$.

Hence we have as our final trial equations

$$[(x^2+y^2)^4+(x^2-y^2)^4]^4=[(x^2+y^2)^4-(x^2-y^2)^4]^4$$
$$+\{2(x^4-y^4)\}^4[\{2xy(x^2+y^2)\}^4+\{2xy(x^2-y^2)\}^4+(x^4-y^4)^4] \quad (5)$$

$$[(x^4+4y^4)^4+(x^4-4y^4)^4]^4=[(x^4+4y^4)^4-(x^4-4y^4)^4]^4$$
$$+\{2(x^8-16y^8)\}^4[\{4x^2y^2(x^4+4y^4)\}^4+\{4x^2y^2(x^4-4y^4)\}^4$$
$$+(x^8-16y^8)^4] \quad (6)$$

$$[(x^2+y^2)^4+(x^2-y^2)^4]^4=[(x^2+y^2)^4-(x^2-y^2)^4]^4$$
$$+\{2(x^4-y^4)\}^4\{(x^4+x^2y^2+y^4)^4+(xy^3)^4+(x^3y)\}^4 \quad (7)$$

$$[(x^4+4y^4)^4+(x^4-4y^4)^4]^4=[(x^4+4y^4)^4-(x^4-4y^4)^4]^4$$
$$+\{(2(x^8-16y^8)\}^4[(x^8+4x^4y^4+16y^8)^4+(8x^2y^6)^4+(8x^6y^2)^4] \quad (8)$$

Of these the first two are immediately to be rejected since they imply (see § 7, equation (5), *infra*)

$$[(x^2+y^2)^4+(x^2-y^2)^4]^4=[(x^2+y^2)^4-(x^2-y^2)^4]^4$$
$$+\{2(x^4-y^4)\}^4(x^8+14x^4y^4+y^8)^2$$

and $[(x^4+4y^4)^4+(x^4-4y^4)^4]^4=[(x^4+4y^4)^4-(x^4-4y^4)^4]^4$
$$+\{2(x^8-16y^8)\}^4(x^{16}+224x^8y^8+256y^{16})^2$$

respectively, equations which are known to be impossible.[1]

The remaining two agree in giving, the former when $x=2$ and $y=1$, the latter when $x=y$,

$$(5^4+3^4)^4=(5^4-3^4)^4+(30)^4(21^4+2^4+8^4)$$

or on removal of the common factor 2 from the roots

$$353^4=272^4+315^4+30^4+120^4,$$

a result which direct calculation will verify. Neither of the equations (7) or (8) however seems to yield any more solutions for other values of x and y; and they must therefore be regarded as, at the best, only more or less likely approximations to an algebraical solution.

N.B.—Hence collecting the results of §§ 2, 3, and 6 we have

$$353^4=315^4+272^4+120^4+30^4$$
$$=300^4+272^4+180^4+150^4+135^4+90^4$$
$$=272^4+252^4+234^4+198^4+189^4+130^4+36^4+30^4$$
$$=300^4+272^4+180^4+150^4+135^4+72^4+72^4+54^4+36^4+36^4;\ \text{etc.}$$

[1] Euler, *Elements of Algebra*, l.c.

§ 7. Finally we may solve the equation

$$P_0^2=P_1^4+P_2^4+\ \ldots\ +P_n^4 \qquad (1)$$

for all values of n greater than 2, when a particular solution is known.

To do this we may employ the method of Diophantos, and take

$$P_0=y_0r^2+x_0r+a_0,\ P_1=x_1r+a_1,\ P_2=x_2r+a_2,\ \ldots,\ P_n=x_nr+a_n.$$

We have then to solve the equation

$$(y_0r^2+x_0r+a_0)^2=(x_1r+a_1)^4+(x_2r+a_2)^4+\ \ldots\ +(x_nr+a_n)^4. \qquad (2)$$

Now if $\quad a_0^2=a_1^4+a_2^4+\ \ldots\ +a_n^4,$

it is clear that on expansion of the square and biquadrates in (2) we can make the coefficients of r and r^2 both vanish by solving linear equations for x_0 and y_0, and therefore on division by r^3, (2) becomes a linear equation in r. The value of r found from this equation with the values of x_0 and y_0 already found substituted in it makes (2) an identity and it is an algebraical solution which clearly presents on integralisation the roots of the biquadrates as functions of the fourth degree in the n variables $x_1, x_2, \ldots, x_n$.

It is further clear that the equation

$$\lambda_0P_0^2=\lambda_1P_1^4+\lambda_2P_2^4+\ \ldots\ +\lambda_nP_n^4 \qquad (3)$$

is in general soluble by the same method if a particular solution is known; thus if $\lambda_0=n$, $\lambda_1=\lambda_2=\ \ldots\ =\lambda_n=1$, we may take as a particular solution $P_0=a^2$, $P_1=P_2=\ \ldots\ =P_n=a$.

For particular values of n, other special solutions of (1) and (3) may be found which will give in general different numerical results from the foregoing.

Thus take the case of (1) when $n=3$. We have identically

$$(a^2u^2+b^2v^2)^2+(b^2u^2-a^2v^2)^2=(au)^4+(bu)^4+(av)^4+(bv)^4. \qquad (4)$$

Let us now choose a, b, u, v so that

$$b^2u^2=(a^2+b^2)v^2.$$

To do this we have necessarily

$$a=x^2-y^2,\ b=2xy$$

so that $\quad 2xyu=(x^2+y^2)v.$

Hence we may take

$$u=x^2+y^2,\ v=2xy$$

and with these values equation (4) becomes

$$(x^8+14x^4y^4+y^8)^2=(x^4-y^4)^4+[2xy(x^2+y^2)]^4+[2xy(x^2-y^2)]^4. \quad (5)$$

Thus $x=2$, $y=1$ gives

$$481^2=12^4+15^4+20^4.$$

Cor. The foregoing result evidently amounts to this, that if $a^2b^2+b^2c^2=c^2a^2$, then

$$(a^2-b^2+c^2)^2=a^4+b^4+c^4.$$

Again, to solve (3) when $\lambda_0=2$, $n=3$, $\lambda_1=\lambda_2=\lambda_3=1$, since

$$a^4+b^4+(a+b)^4=2(a^2+ab+b^2)^2,$$

replacing a and b, each by its square, we have

$$a^8+b^8+(a^2+b^2)^4=\tfrac{1}{2}[a^4+b^4+\overline{a^2+b^2}]^2.$$

If then we put $a=x^2-y^2$, $b=2xy$, this becomes

$$\begin{aligned}&(x^2+y^2)^8+(2xy)^8+(x^2-y^2)^8\\&=\tfrac{1}{2}[(x^2-y^2)^4+(2xy)^4+(x^2+y^2)^4]^2\\&=2(x^8+14x^4y+y^8)^2\\&=2[\{x^4-y^4\}^4+\{2xy(x^2-y^2)\}^4+\{2xy(x^2+y^2)\}^4] \quad (6)\end{aligned}$$

by (5) above. Thus $x=2$, $y=1$ gives

$$3^8+4^8+5^8=2(12^4+15^4+20^4)=2\cdot 481^2.$$

The last part of (6), which is simply a solution of

$$a^8+b^8+c^8=2(a^4b^4+b^4c^4+c^4a^4),$$

is immediately obtained otherwise. For if a, b, c be integers connected by the equation $a^2+b^2=c^2$, we have, on squaring each side of this equation

$$a^4+b^4-c^4=-2a^2b^2,$$

and on again squaring we obtain

$$a^8+b^8+c^8=2(a^4b^4+b^4c^4+c^4a^4)$$

which is the required result if we put $a=x^2-y^2$, $b=2xy$, $c=x^2+y^2$ to make $a^2+b^2=c^2$. Corresponding results may naturally be obtained by squaring any identity of the form $\lambda x^2+\mu y^2=\nu z^2$.

But for all values of n greater than 4, a single algebraical

formula can be found to satisfy equation (1). For we have identically

$$(t^2+z^4)^2=t^4+(z^2)^4+2t^2z^4.$$

If then we put $t=x^2+xy+y^2$ this becomes

$$[(x^2+xy+y^2)^2+z^4]^2=(x^2+xy+y^2)^4+(z^2)^4+z^4[x^4+y^4+\overline{x+y^4}]. \quad (7)$$

Since x and y are arbitrary we may take (as in § 4 *supra*)

$$x=Q_1,\ y=Q_2,$$

where Q_1 and Q_2 are algebraical quantities satisfying the equation

$$Q_1^4+Q_2^4=P_1^4+P_2^4+\ \ldots\ +P_r^4$$

where r is greater than 2. Hence (7) becomes

$$[(Q_1^2+Q_1Q_2+Q_2^2)^2+z^4]^2=(Q_1^2+Q_1Q_2+Q_2^2)^4+(z^2)^4+\{z(Q_1+Q_2)\}^4 \\ +z^4(P_1^4+P_2^4+\ \ldots\ +P_r^4)$$

which gives a square equal to the sum of 5 or any greater number of biquadrates.

ROBERT NORRIE

THE PROBLEM OF PARTITION OF ENERGY, ESPECIALLY IN RADIATION

1. AGREEMENT seems to be nearly as remote as ever regarding the manner in which deviation from the condition of equipartition of energy amongst the various freedoms of an apparently conservative system, in apparent equilibrium, is brought about. The well-known discrepancies which occur between the actual ratios of the principal specific heats of gases and their theoretical ratios calculated, on the assumption of equipartition, from the multiplicity of freedoms which radiational phenomena make evident in the case of even monatomic gases, make the fact of extreme deviation from equipartition very evident.

It is fully recognised that, in many very special cases, dynamical freedoms may be entirely inoperative. So one way of avoiding the difficulty consists in asserting that the special freedoms made evident in radiational phenomena are inoperative in ordinary thermal phenomena. Such a mode is unsatisfactory apart from the specification, by analogy at least, of an appropriate mechanism; for the doctrine of equipartition does not permit mere partial inoperativeness—the inoperativeness must be total. Another method, adopted by Jeans, consists in regarding a final condition of statistical equilibrium between matter and ether, with consequent equipartition of energy amongst the freedoms, as unattainable in finite time; so that the practical 'steady' conditions, which subsist in experimental tests, and are the result of a steady supply of energy in one form compensating an equal steady loss in an other form, give rise to that non-equable

partitioning of energy amongst wave-lengths which is expressed by Planck's well-corroborated law. A third method, that of Planck, locates the source of non-equipartition in the intrinsic nature of energy itself, which is postulated to be atomic, the ultimate unit being so large that it may only be manifested in relation to many degrees of freedom, some freedoms absorbing no units, others one unit, and so on.

2. Planck's postulate has the merit of leading to a well-supported expression for the distribution of energy amongst the various wave-lengths in 'natural' radiation; it has the possible demerit of necessitating discontinuities of motion on molecular, atomic, or, at any rate, on 'freedomal' scale. Yet it may be that the seeming demerit is not real, the discontinuities vanishing as a matter of statistics.

Sir J. Larmor, in his recent Bakerian Lecture (*Proc. R.S.*, 1909, vol. lxxxiii.), modifies and amplifies Planck's treatment in such a way as to get rid of the assumption of the finitely atomic nature of energy. Indivisibility of an element of energy is replaced by an unalterable ratio of the element of energy of any one type to the extent of a 'cell,' of corresponding type, in which that element is contained. The actual element itself may be infinitesimal, so motional discontinuities become infinitesimal. A 'cell' replaces the 'degree of freedom' of the previous treatment, and each cell is of equal opportunity or extent as regards an element of disturbance, which may pass from one cell to another of a different type, the amount of energy associated with it being possibly altered in the process. Thus—in analogy with the passage of heat energy in diminished (or increased) amount from a region of high to one of low temperature (or conversely), in association with the necessary performance (or absorption) of external work—we have the transformation of radiation from one wave-length to another in association with the performance or absorption of work. These postulates lead to Planck's law, the constants only having important modifications of meaning.

3. Jeans has recently discussed Larmor's view, and arrives at the conclusion (*Phil. Mag.*, Dec. 1910) that it is neither possible to avoid finiteness of the element of energy nor ultimate discontinuity of ether structure in relation to radiation if Planck's law corresponds to the true final condition of equilibrium. That is to say, radiation can only be regarded as capable of existing in the ether in amounts which are multiples of a finite unit.

While Jeans' own view (§ 1) must be recognised as indicating a possible solution of the fundamental difficulty regarding the partition of energy, it is not possible, because of our ignorance of the intrinsic nature of matter, of ether, and of the connection between these, to be quite certain that Larmor's view, or even Planck's, is inadmissible. It is not inconceivable that the nature of these entities may impose identity between the distribution which obtains in the steady state under experimental conditions, and that which would obtain in the final state of a strictly conservative system. I venture therefore to indicate the following mode of considering the problem. It leads to an expression which differs slightly in form from that of Planck, but which can practically be identified with it throughout the range of observed wave-lengths, and which with it reduces to Rayleigh's form when the wave-length is of suitable magnitude.

4. Interchange of energy amongst freedoms of the same type constitutes ordinary transmission of energy of the type involved; interchange of energy amongst freedoms of distinct types constitutes that transmission of energy which is ordinarily called transformation. When different subsystems, in the equilibrium condition, are freely open to interchanges of energy, a universal generalised temperature or potential, possessing a definite statistical value throughout the total system when that system possesses a definite total amount of energy, must exist.

Let there be altogether ν subsystems, let $N_1 \ldots N_\nu$ be

the respective numbers of freedoms in these subsystems, and let $c_1 \ldots c_\nu$ be the respective capacities of these subsystems for energy. If P is the equilibrium value of the universal potential, the amounts of energy, $E_1 \ldots E_\nu$, in each subsystem are $c_1P \ldots c_\nu P$ respectively. As in Boltzmann's treatment, the equilibrium state is the most probable state; and so, following Planck's modification of that treatment, the probability being estimated by the number of ways in which cP units of energy can be contained in N freedoms, we obtain as the condition of equilibrium the equation

$$\sum_1^{m\nu} \log \frac{N_m + c_m P}{c_m P} d \cdot c_m P = 0 \quad . \quad . \quad . \quad (1)$$

Now, in the condition of statistical equilibrium, as in the approach to it, there is constant transmission of energy from one subsystem to another; and the energy tends to accumulate in those subsystems from which the rate of transmission is slowest. Hence the total rate of transmission tends to a minimum. So, $r_m c_m P$ being the rate of transmission from the subsystem m, we have, if the r's are constant,

$$\sum_1^{m\nu} r_m d \cdot c_m P = 0 \quad . \quad . \quad . \quad . \quad (2)$$

These two conditions imply nothing more regarding the potential P than that it is statistically uniform throughout the total system. It might be slowly varying with time. If we further add the condition of conservation of energy, we get

$$\sum_1^{m\nu} d \cdot c_m P = 0 \quad . \quad . \quad . \quad . \quad (3)$$

The three equations give

$$E_m = c_m P = \frac{N_m}{\epsilon^{a+br_m} - 1} \quad . \quad . \quad . \quad (4),$$

where a and b are functions of P alone. The simplest admis-

sible conditions are $a=\alpha P^{-1}$, $b=\beta P^{-1}$, where α and β are absolute constants, in which case (4) becomes

$$E_m=c_mP=\frac{N_m}{\epsilon^{\frac{\alpha+\beta r_m}{P}}-1} \quad . \quad . \quad . \quad (4a)$$

5. To apply this expression to the case of radiation we have to evaluate $E_m r_m=E_\lambda$, the energy transmitted per second per unit range of wave-length in the neighbourhood of wave-length λ. We must therefore either appeal to experiment for the determination of the appropriate forms to be given to N_m and r_m in terms of λ, or we must determine these by means of suitable assumptions regarding ether and matter and their connection. Thus if we assume that the fractional rate of transmission of the energy content of each freedom is identical per vibration, the fractional rate of transmission per unit of time is proportional to the frequency, so that we can write $\beta r_m=\gamma\lambda^{-1}$, γ being an absolute constant. The value of N_m, when the frequency is not too small, is given by Rayleigh's reasoning (*Sc. Papers*, vol. iv. p. 484, or *Phil. Mag.*, xlix. p. 539, 1900) as $A\lambda^{-4}$, where A is a universal constant. Hence

$$E_\lambda=\frac{A\lambda^{-5}}{\epsilon^{\frac{\alpha+\gamma\lambda^{-1}}{P}}-1} \quad . \quad . \quad . \quad . \quad (5),$$

an expression which, with Wien's displacement law holding, gives the well-known experimental result that the maximum energy is proportional to the fifth power of the absolute temperature provided that the latter be identified with P. The expression becomes identical with Planck's so long as $\alpha\lambda$ is negligible relatively to γ. We must therefore recognise that this restriction holds throughout the range of wave-length to which Planck's formula is applicable. Outside that range the quantity E_λ becomes very small.

If, within that range, $P\lambda$ becomes large relatively to γ,

the expression (5) reduces to $A\gamma^{-1}.P\lambda^{-4}$, which is the form given by Rayleigh as applicable when $P\lambda$ is sufficiently large while λ is not too large. When λ is very large with P not too small, (5) takes the form $A\alpha^{-1}.P\lambda^{-5}$.

6. The distinction between energy transmitted by, and energy stored in, definite freedoms is of fundamental importance. The equation (4*a*) shows that there is not universal equipartition of the energy allotted to all freedoms except under the condition that βr_m is negligible relatively to α; while, on the other hand, there is equipartition universally amongst the energies transmitted per unit of time if βr_m is large relatively to α and small relatively to P.

The ratio of the energy transmitted per unit of time per degree of freedom to the energy stored in that freedom takes here the place of the element of energy, and there is no limitation upon its finitude. There is necessarily equipartition of energy amongst all freedoms for which it has one and the same value.

WILLIAM PEDDIE

ON THE ACCURACY ATTAINABLE WITH A MODIFIED FORM OF ATWOOD'S MACHINE

Introduction

A careful determination of g by means of the ordinary type of Atwood's machine does not, as a rule, lead the average student in a physical laboratory to a better result than 930 or 940 cm/sec^2. From the point of view of successful teaching, it is somewhat unfortunate that, after bestowing reasonable care and attention to his work, a student should be unable to obtain a result approximating satisfactorily to what he knows to be the correct figure. Not unnaturally, he takes it for granted that the actual numerical result obtained from his experimental labours is quite immaterial as long as the processes involved are clearly comprehended, and to him experimental physics is anything but an exact science. On the other hand, to set before the ordinary student a complicated apparatus specially designed for reaching an accuracy of 0·1 per cent. would be proceeding to the other extreme, and one could hardly expect much benefit to be derived from its use. But even the student who has already had some experimental training, and who has realised that quantitative relationship is just as important as qualitative, could not do any better in this case, for the defects are inherent to the method usually followed of timing the fall through a distance of 150 or 200 cm. with a metronome or stop watch: in his interests, at any rate, a more accurate procedure should be adopted.

The purpose of the present paper is to show how the usual type of Atwood machine may very readily be modified so as

to give synchronous chronographical records of both time and distance at various points of the fall. The apparatus was, in fact, devised in the course of a research upon the wind-pressure law and the efficiency of air-drags, for the purpose of obtaining accurate time-distance curves for the fall of a parachute. Some results of this research will soon appear; but as the calibration of the apparatus showed that it could be used with tolerable accuracy for the determination of g, it seemed desirable to publish a description of it, along with a few examples of the degree of accuracy that may be reached with it. The results here appended are not to be taken as giving the limits of accuracy of the method, for, unfortunately, the construction of the friction rollers in the apparatus used is not quite satisfactory, with the result that friction is somewhat variable and in need of constant evaluation: with a more carefully constructed apparatus friction would be much smaller, and its constancy more assured.

Description of Apparatus

A six-spoked aluminium wheel, cut with a V-groove in the rim, and mounted on a steel spindle, runs on four aluminium friction rollers. These rollers have conical sockets and are mounted on points screwed into a brass plate, so that if the steel spindle were completely homogeneous and were laid on the rollers, electrical contact would be complete from one side of the apparatus to the other during one whole revolution of the wheel. At one end of the spindle, however, a semi-cylindrical portion of the steel is removed and replaced by an identical piece of hard ebonite, the whole being then turned true in the lathe; it follows that at a certain point during each revolution the ebonite is in contact with both friction rollers on which it rests, and at that moment electrical contact is no longer possible between the two sides of the apparatus. Hence, by connecting with a chronograph, a single record is

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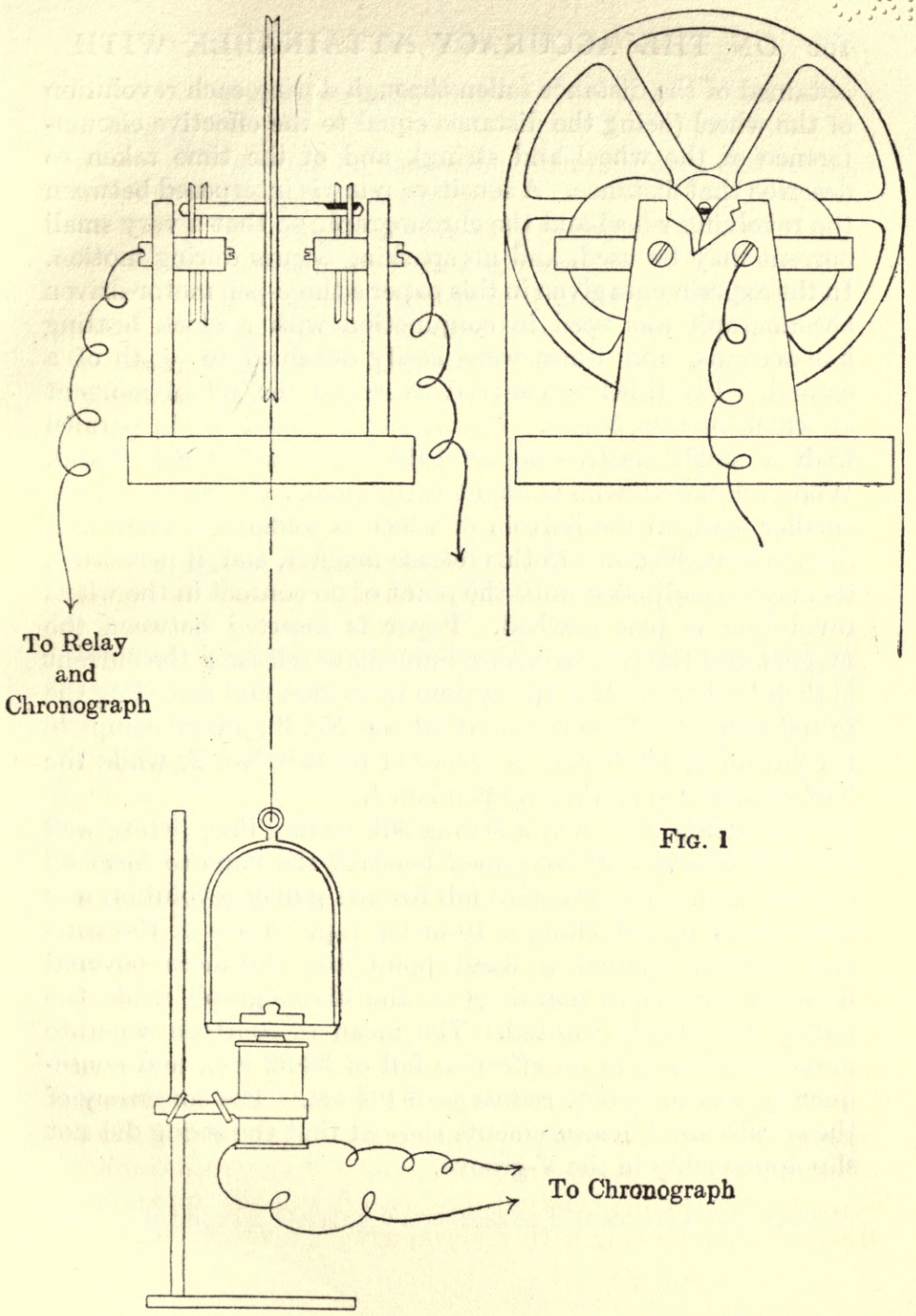


FIG. 1

obtained of the distance fallen through during each revolution of the wheel (being the distance equal to the effective circumference of the wheel and string), and of the time taken to describe that distance. A sensitive relay is interposed between the revolving wheel and the chronograph, so that a very small current may be used, and no sparking occurs during motion. In the experiments given in this paper a three-pen motor-driven chronograph was used in conjunction with a clock beating half-seconds, and times were easily obtained to $\frac{1}{100}$th of a second. The third pen served to record the actual moment at which motion began. Its magnet is connected in parallel with a small electro-magnet held in an adjustable stand. When an experiment is about to be made, the pan with the smaller load, to the bottom of which is soldered a small iron disc, is brought down to this release magnet, and, if necessary, its height is adjusted until the point of no contact in the wheel revolution is just reached. Paper is inserted between the magnet and the pan to ensure immediate release ; the current is then broken, setting the system in motion and recording the initial point of the experiment on pen No. 3 ; every complete revolution of the wheel is recorded on pen No. 2, while the half seconds are marked by pen No. 1.

The string used was a strong silk fishing line, fitting well into the groove and continued beneath the pans to form an endless loop. The effective fall for one pulley revolution was determined by attaching a 10-metre tape to one of the pans and reading against a fixed point the distances covered between successive markings of the chronograph while the pulley was slowly rotated. The mean of fourteen separate measurements gave an effective fall of 38·92 cm., and consequently a mean pulley radius $p=6{\cdot}194$ cm. The constancy of these individual measurements showed that the string did not slip appreciably in the V-groove.

Dynamical Equations and Data

Putting

L=load on each side, including pans and string,
w=driving weight,
P=weight of revolving pulley,
p=effective radius of pulley,
k=radius of gyration of pulley,
a=observed acceleration,
a=radius of spindle,

and $a \sin \lambda$=effective friction radius,

the friction moment becomes $2L+P+w\left(1-\frac{a}{g}\right) a \sin \lambda$, and we readily obtain the well-known result

$$g=\frac{a\left[2L+w\left(1-\frac{a}{p}\sin\lambda\right)+P\frac{k^2}{p^2}\right]+g\frac{a}{p}\sin\lambda[2L+w+P]}{w}. \quad . \quad (1)$$

Frictional retardation, a', is determined by observing the time taken to come to rest after communicating a certain speed to the system symmetrically loaded. This is also done on the chronograph, it being now necessary to observe and record on pen No. 3 the moment at which motion *ceases*. To get as near as possible to the same conditions of load as those obtaining in the actual a experiment, it is well to observe a' with a load $L'=L+\frac{w}{2}$ on each side, and in that case a' is given by

$$\frac{g\frac{a}{p}\sin\lambda[2L+w+P]}{2L+w+P\frac{k^2}{p^2}}$$

Hence equation (1) reduces to the very simple form

$$g=\frac{a+a'}{w}\left[2L+w+P\frac{k^2}{p^2}\right] \quad . \quad . \quad . \quad (2)$$

In this form, viz. Driving Force *minus* Frictional Force *equal to*

Effective Force, the meaning of the equation can be grasped even by a student whose dynamical knowledge is small.

With the present apparatus it was found necessary to determine a' several times before and after each determination of a; with an apparatus of more satisfactory construction this would probably be unnecessary.

To get k, the radius of gyration, the pulley wheel was removed from its position on the friction rollers and was attached to bi-filar suspensions. Three separate determinations gave $k=4{\cdot}221$, $4{\cdot}205$, 4.230, giving a mean $k=4{\cdot}218$. This, with the weight $P=44{\cdot}0$ g, and the radius $p=6{\cdot}194$ cm., gives for the equivalent mass of the pulley $P\frac{k^2}{p^2}=20{\cdot}5$ g.

The inertia of the four friction rollers was found from their dimensions and their weights to be one-tenth of that of the pulley wheel itself. As their angular speed is less than one-tenth that of the pulley, their total kinetic energy is less than one-thousandth of the kinetic energy of the pulley, and has therefore been left out of account in the subsequent calculation of g.

A graphical evaluation of $P\frac{k^2}{p^2}$ made in the usual way from the results appended, by plotting $\frac{w}{a+a'}$ against $2L+w$ and reading off the intercept on the load axis, led to a value $21{\cdot}2$ g.

A graphical method may also be adopted for ascertaining the fraction of a revolution at the beginning in finding a, and at the conclusion in finding a'. If R is the number of revolutions from and to rest respectively, we have $\frac{R}{T^2}$ in each case a constant, and so x, the unknown fraction of a revolution, can be at once obtained by plotting (0, 1, 2, 3, etc.) R against T_0^2, T_1^2, T_2^2, T_3^2, etc., where T_0, T_1, etc., are the times of x, $1+x$, $2+x$, etc., revolutions. In the a measurements this fraction is

reduced to the smallest possible value by initial adjustment of the level of the release magnet, but one has no control over its value in the a' determinations. As a rule, however, it is not necessary to evaluate x, the incomplete part of a revolution, in the determination of a and a'; it is sufficient to plot squares of times from beginning and end respectively against number of complete revolutions, and the products of the slopes of the resulting straight lines into twice the effective distance of one revolution at once give the acceleration and retardation required. This was the procedure adopted in obtaining the results communicated in this paper: the experimental points, as long as the speed did not become excessive, lay exactly on a straight line, whose slope could easily be found to 1 in 1000.

The weight of the two pans and string used in the following experiments was 87·5 g, while additional loads of 50, 100, 150, and 200 g were added to each side. In each case two driving weights were tried, viz. 10 g and 20 g. The chronograph clock was carefully calibrated, giving a mean nominal second equivalent to 0·995 true seconds.

The maximum fall available was about 700 cm., but although records were obtained for the complete fall in every case, the $s-t^2$ curves showed some curvature for the last few metres of fall, and in the case of large acceleration this curvature was quite pronounced, the acceleration in every case diminishing as the speed increased. This is obviously due to the resistance of the pans to motion through the air, and, in fact, the apparatus is used chiefly for the determination of these resistances with larger surfaces. The resistance was allowed for in the present experiments by using for the determination of a only the first part of the fall, where the speed was low and the graph was accurately straight; should it be desired to use it over greater distances, it would be well to dispense entirely with pans, and to use weights made in the form of rods, so that the area presented normally to the direction of motion would be a minimum.

Results

The following are eight different values of g obtained by the method indicated above. The experiments are grouped in pairs, at the beginning and end of which a' was determined a few times, the mean of each set being taken as holding for the actual experiments.

Values of g determined with Modified Form of Atwood's Machine

$2L$ gram.	a' cm/sec^2.	w gram.	$2L+w$ gram.	$2L+w+P\frac{k^2}{p^2}$ gram.	a cm/sec^2.	g cm/sec^2.
187·5	3·49	10	197·5	218	41·37	978
		20	207·5	228	82·00	975
						..976
287·5	3·64	10	297·5	318	27·16	979
		20	307·5	328	56·19	981
						..980
387·5	3·56	10	397·5	418	19·96	983
		20	407·5	428	42·35	983
						..983
487·5	3·31	10	497·5	518	15·65	982
		20	507·5	528	33·75	978
						..980
					Mean value of g.....980	

Discussion of Results

Considering the magnitude of the frictional correction for the particular apparatus used in these experiments and the slight uncertainty in its numerical value, the remarkably good mean value obtained for g must be regarded as somewhat

fortuitous. That there are irregularities is evident from the above values of a', which, as a' varies as $\left[1+P\frac{1-\frac{k^2}{p^2}}{2L'+P\frac{k^2}{p^2}}\right]$, should decrease asymptotically as the load increases; but it would also seem that the effect of these disturbances can be determined by a proper evaluation of friction for each individual experiment. No doubt, more carefully constructed friction rollers would prove more regular in action; but as the accuracy here attained is more than sufficient for the author's immediate purpose, he did not think it necessary to have another wheel constructed in order to be able to test this point further.

It is, perhaps, of interest to examine under what conditions greatest accuracy may be attained. For a given absolute possibility of time measurement a should be as small as possible in order that it should be known with the highest relative accuracy, but then the difficulty arises that a' is a large fraction of the total, and any slight uncertainty in its value affects the result accordingly. On the other hand, to increase a so as to make a' relatively small would entail less accuracy in the time measurement, the square of which is involved, and, moreover, air resistance at such comparatively high speeds would become appreciable even during the earlier stages of the fall. It is, perhaps, significant that the worst value amongst the foregoing results is that obtained from the greatest acceleration. What should be attempted, therefore, is the reduction of the absolute value of a' to a minimum. Since $a'=g\frac{a}{p}\sin\lambda\left[1+P\frac{1-\frac{k^2}{p^2}}{2L'+P\frac{k^2}{p^2}}\right]$, for a given load L', with P fixed by considerations of stability, the desired result will be attained

by making a and λ a minimum, and k as nearly equal to p as possible. This means that the supporting pivots must be thin and well lubricated, and that the mass of the pulley must be concentrated in the rim, the spokes being as light as possible, consistent with the load they have to bear.

In conclusion, it might be well to draw attention to the fact that the only modification in the usual type of ATWOOD pulley necessary to adapt it to the foregoing method is the very simple one of forming the wheel spindle partly of metal and partly of non-conducting material. Before the plan described above was adopted, the effect was tried of coating half of one end of the spindle with a very thin layer of hard varnish. This answered the purpose sufficiently well for one or two experiments, but the varnish soon cracked in places, giving rise to confused records on the chronograph. Something more permanent is required.

When the apparatus is to be used as an ATWOOD machine for determining the acceleration due to gravity, an inking chronograph is not at all essential; in fact, the accuracy of the time measurement obtained with the simpler forms, in which a smoked plate travels or a smoked drum revolves in front of a vibrating tuning fork, would reach the order of 1/500th second. Most laboratories now possess such a chronograph in their equipment, and most students are called upon to use it at some stage of their laboratory experience; and as equation (2), containing the dynamics of the method, is extremely simple, there is no reason why any junior student should be unable to apply it; the extra knowledge of experimental work required is but small, while the resulting gain in accuracy is great.

JOHN PATRICK DALTON

THE DEVIATION OF THE OSCILLATIONS OF A VISCOUS SOLID FROM THE ISOCHRONOUS LAW

THE fact of the distinct departure from isochronism of the torsional vibrations of a metallic wire has been known since the classical researches of the Russian physicist Kuppfer were published in the middle of last century. And that fact, amongst others, exhibits the essential difference existing between the origin of the internal dissipation of energy in this case and that which is effective in cases of true viscosity, in spite of the other fact, established by Kelvin and very rigidly corroborated by Tomlinson, that the logarithmic law applies to the decay of the small oscillations of a metallic wire.

When the oscillations are large the logarithmic law of decay is widely departed from, and the range of oscillation y is, to a high degree of approximation, related to the time x by the condition

$$y^n(x+a)=b,$$

where n, a, and b are constants throughout a large series of oscillations (see Mr. Ritchie's paper in this volume, p. 113).

Further, the departure from the sine law during any single oscillation is very marked. The time of inward motion from the maximum elongation to the zero point is greater than the time of outward motion from the zero point to the maximum (*Trans. Roy. Soc. of Edin.*, 1896). In this note I propose merely to indicate, by the aid of a diagram, the nature and extent of these deviations; a full descriptive and theoretical

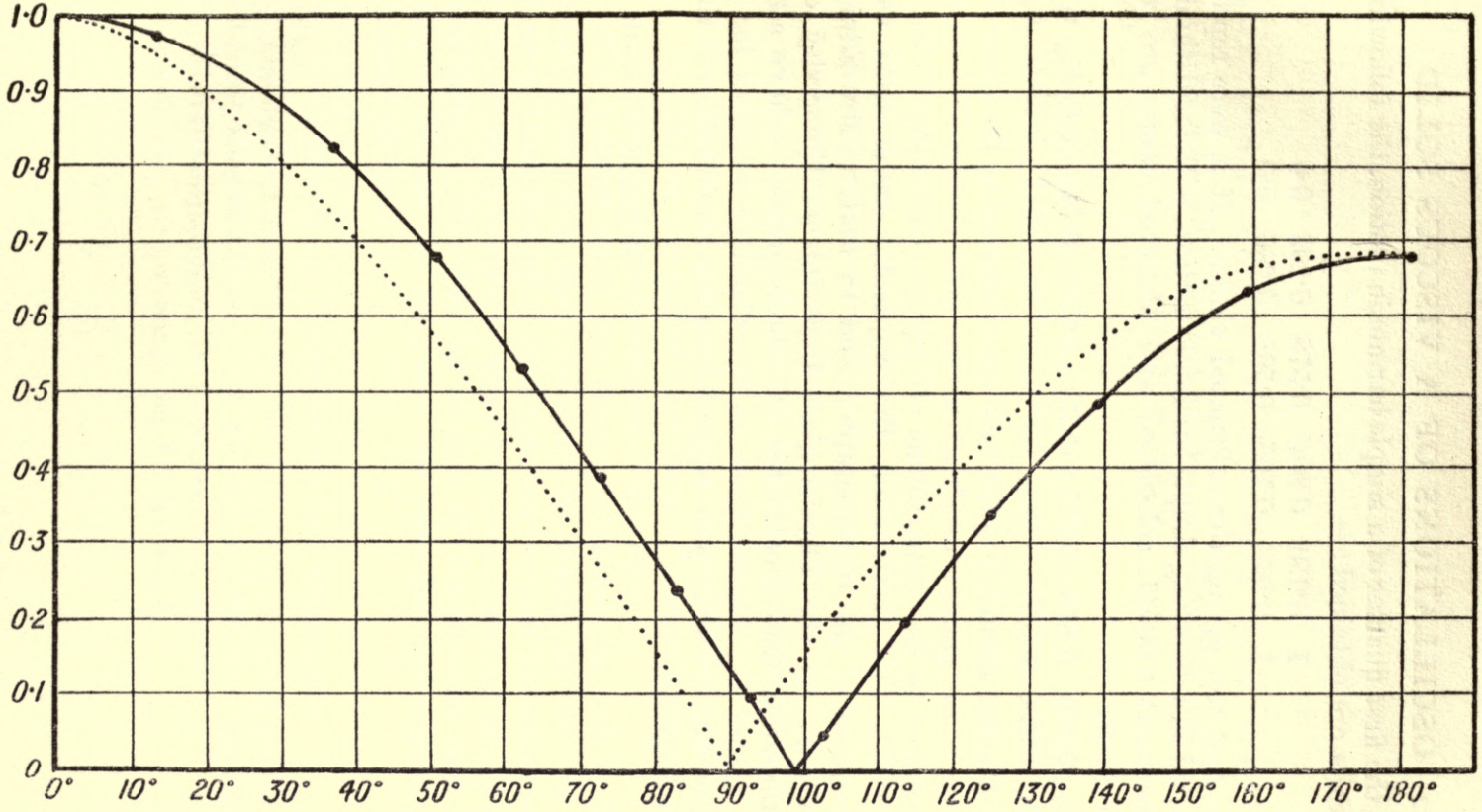
account will be communicated to the Royal Society of Edinburgh.

The wire to which the diagram refers was one of soft copper, No. 19 B.W.G., and 22·5 cm. in length. The oscillator was in the form of a brass ring, from which brass teeth, arranged at equal angular intervals, projected downwards. These teeth, as the ring revolved, made contact with radial mercury pools in an ebonite plate below. These pools were also arranged at equal angular intervals, but the interval between them was different from that between successive teeth, so that the principle of the vernier came into play. The contacts so made completed electric circuits, by means of which chronographic records were obtained of the instants at which the contacts occurred. It was possible in this way to make records of the position of the oscillator at successive intervals of 2° throughout its range. In the special experiment here described much fewer observations were sufficient, and so records were taken at intervals of 12°.

The full curve in the diagram is drawn through the recorded points, and represents the course of an oscillation from the first positive to the first negative elongation, negative values being plotted as if they were positive. In that single half-oscillation the amplitude dropped by nearly one-third of its initial value. Times are represented as angles, the complete time of the half-oscillation being 180. The time of the inward oscillation exceeds that of the outward oscillation by nearly one-fifth of the mean value of the two.

The dotted curve represents the course which would have been followed had the drop of amplitude been due to a true viscous resistance.

It follows that any representation of the outward or inward motions separately, either as unresisted simple harmonic, or as viscously resisted harmonic, motion, is of no real value. Yet the comparative accuracy of these empirical representations is of some interest. If the inward motion is represented


1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0
0°
10°
20°
30°
40°
50°
60°
70°
80°
90°
100°
110°
120°
130°
140°
150°
160°
170°
180°

as the first quarter of a simple harmonic motion, the following results are obtained:—

1	0·950	0·804	0·578	0·293	0·0
1	0·948	0·795	0·568	0·280	0·0

the first row giving the calculated values. If it were represented as a decaying simple harmonic motion, with logarithmic decrement 0·00441, calculated and observed values are respectively:—

1	0·969	0·816	0·675	0·531	0·393	0·248	0·0995	0
1	0·974	0·825	0·681	0·534	0·390	0·241	0·0990	0

For the accuracy which has been obtained in the observations I am greatly indebted to the skill of Mr. J. Linton, mechanic to the Department of Physics, University College, Dundee, who constructed the apparatus used, with the exception of the chronograph; and to that of Mr. Ednie, mechanic to the Physiological Department, University of Edinburgh, who constructed the chronograph. I have also to record my indebtedness to the Carnegie Trustees for a grant which was in part expended on the construction of the chronograph.

William Peddie

THE DISSIPATION OF ENERGY AND OTHER EFFECTS OBSERVED IN TORSIONAL OSCILLATION

In the determination of the law of decrease of torsional oscillations of an iron wire, when the range of oscillation is large in comparison with the palpable limits of elasticity, an equation of the form

$$y^n(x+a)=b$$

has been shown by Dr. Peddie (*Phil. Mag.*, July 1894) to give close representation of results where—

y=the range of oscillation,

x=the number of oscillations since the commencement of observations,

n, a, b=quantities, constant for any one experiment, depending on the initial conditions of the experiment and the previous treatment of the wire.

The present work has been undertaken to find if this equation can with equal accuracy be applied in the case of wires of brass and other materials, and to find the effect produced on the constants of this equation by altering the initial conditions of the wire by change of temperature and by fatigue induced in the wire by repeated extensional or torsional strains.

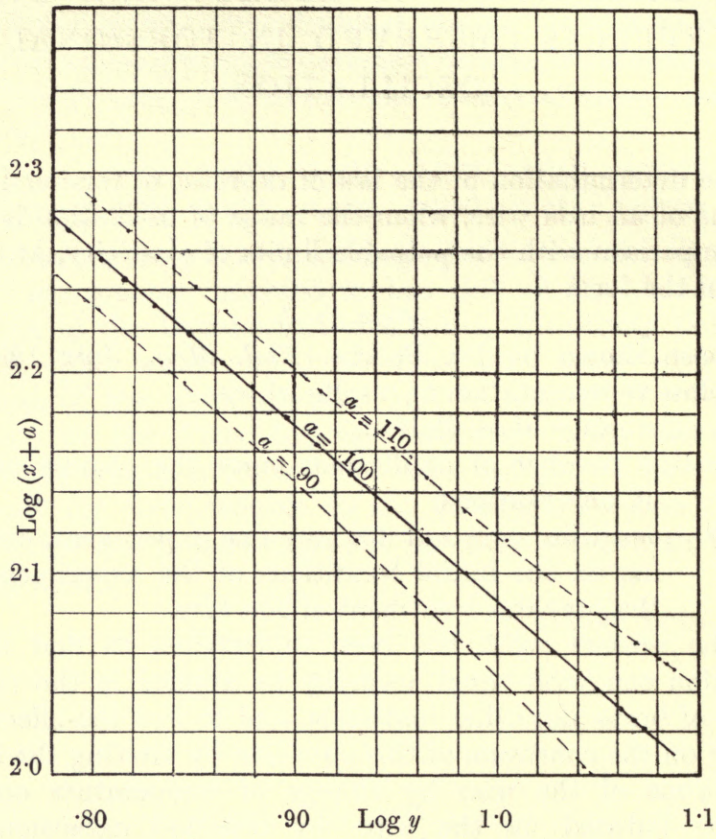
Method of Calculating the Constants

The method described by Dr. Peddie in a second paper on the same subject (*Trans. Roy. Soc. Edin.*, 1896) was employed for the determination of the quantities n, a, and b.

Since $$n \log y+\log (x+a)=\log b,$$

then if log $(x+a)$ be plotted against log y, the corresponding points will lie on a straight line which intersects the axis

FIGURE 1—Brass at 275° C. $a=100$ $n=\cdot 86$



along which log y is measured at an angle whose tangent is n, provided that the proper value of a be inserted. The actual value of this constant to be added to x depends upon the interval which elapses after starting the experiment until the first reading is taken. A rough idea of the value of a to be taken is got from the curve with scale readings as ordinates and number of oscillations as abscissæ, when the distance

from the y axis of the line which the curve approaches asymptotically gives the value of a. If a wrong value of a be taken, the points in the curve of log y against log $(x+a)$ will not lie in a straight line, a curve convex to the origin being obtained if the value of a be too large, and a curve concave to the origin if the value of a be too small. This is seen [1] to be the case in figure 1, when with $a=90$ the curve is concave, and with $a=110$, convex. The value of a which gives the straightest line is taken, and from the tangent of the angle included by the line and the axis along which log y is measured n is found, and b can then be got by substitution.

Method of Conducting the Experiment

The wire under consideration was suspended from a clamp attached to a torsion head, and at the other end was clamped, symmetrically and horizontally, a heavy lead ring of large moment of inertia. To the outer surface of this ring was fastened a scale divided into millimetres. The vibrations of the apparatus were damped out, and the torsion head then carefully turned so that no pendulum oscillation should be set up in the wire. Exterior disturbances were also, as far as possible, avoided. Readings of successive maxima ranges of oscillation were taken by means of a telescope with cross wires inserted, the crossing point being fixed in the same horizontal plane as the lead ring, at a distance of about 6 feet from the scale. It was found convenient to miss the first reading, and to take readings at the end of every oscillation after the first until ten oscillations had been completed, and thereafter to take readings after every fifth oscillation. Except in the case of tin wire, in which case the oscillations died down with extreme rapidity, the readings were extended over a hundred oscillations. The zero of the scale was found by taking successive readings to right and left at intervals,

[1] The scale readings y on the diagrams correspond to a rotation through 1° per ·175 cm. of scale.

and the average of these values was then taken. A curve drawn with the scale readings as ordinates and the number of swings as abscissæ showed by means of the waviness of the curve if ordinary pendulum oscillations had been appreciably started in the apparatus. The values of log y were then plotted against those of log $(x+a)$, and when the proper value of a had been found, so that the points lay practically on a straight line, the constants were obtained.

Confirmation of the Empirical Law

Wires of nine different metals were tested, brass, copper, aluminium, tin, zinc, silver, german silver, platinum, and nickel. Of these, brass, tin, zinc, silver, german silver, and nickel were found at the ordinary temperature to give close agreement, over the very large range of oscillations taken, to the general law, in each case a suitable value of a being found which caused all the points to lie on a straight line. It was found, however, that in the case of the remaining metals, and especially in the cases of aluminium and copper, no one value of a could be found to bring all the points into one line, an s-shaped curve being obtained in general. When this was first observed, it was thought that the law did not hold in such cases, or at least that it did not hold over the range taken. In attempting to straighten, in this case, one part of the curve, however, it was found that, with a certain value of a the points could be brought to lie on *two* straight lines inclined at an angle not differing much from 180°. It was further found that this could not be done in every case with the same value of a for the two portions, but, by choosing a slightly different value of a, in every case the points could be brought to lie on two straight lines. The doubling of the line, as will be seen when the metals are considered separately, was found to depend upon controllable conditions, *e.g.* in brass it occurred when the metal had been brought to a certain temperature in the neighbourhood of 375° C. In

most cases it was found that the value of n was greater in the line drawn through the points corresponding to the smaller oscillations.

Experiments on Brass Wire

In the present series of experiments brass was the material most studied in detail, and, for the purpose of experiment, lengths of brass wire, approximately one millimetre in diameter,[1] were used. The length was in each case chosen so that, from clamp to clamp on the torsion apparatus, there should be exactly one foot of wire. It was found in a subsequent experiment, however, that change of length had no effect on the constants a and n, although b might differ considerably. In an experiment on 6 inches of brass wire, the values of a and n were found to be equal to those got with 12 inches of the same wire. The reason can readily be seen, as follows.

If we postulate that the loss of potential energy in a breaking down of molecular groups is proportional to a power of the angle of torsion, we can approximately write (Peddie, *Phil. Mag.*, July 1894) the loss of energy per swing in the form $-kydy=py^m dx$.

Now, in a wire of half length, k is doubled for the same value of y; and the loss of energy, with the same y at half length, is half of what it would have been in the wire of whole length at $2y$. But in the wire of whole length at $2y$ the loss is

$$p2^m y^m dx.$$

Thus
$$-2kydy=p2^{m-1}y^m dx$$
$$-kydy=p2^{m-2}y^m dx,$$

so
$$y^{m-2}(x+a)=\frac{k}{2^{m-2}p(m-2)},$$

i.e.
$$y^n(x+a)=\frac{k}{pn}\cdot\frac{1}{2^n}$$
$$=b'=b\frac{1}{2^n}.$$

[1] ·0975 cm.

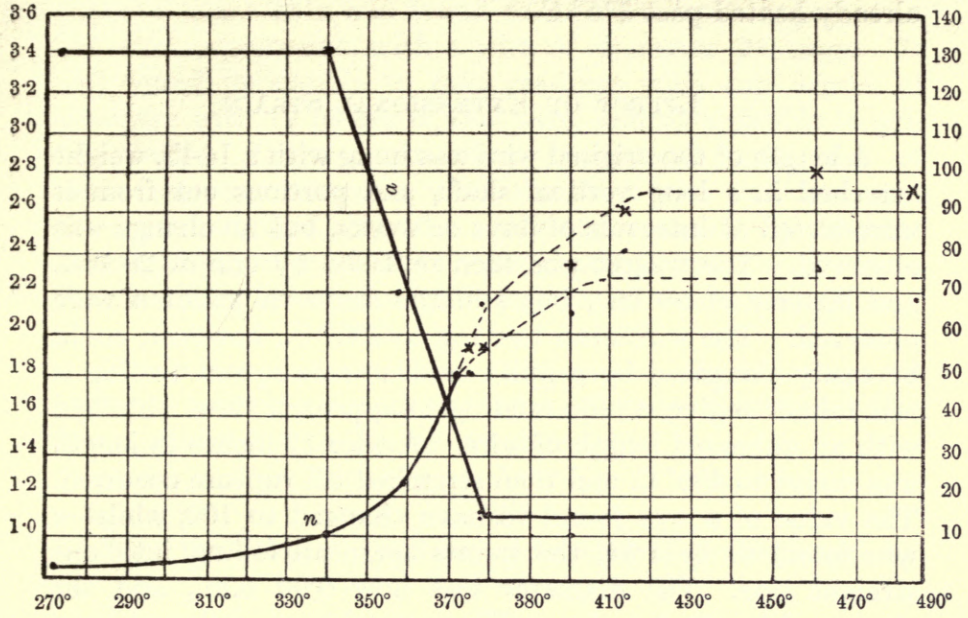
The empirical law was found to hold over a very long range at the ordinary temperature. In all cases the points lay, with the proper value of a, in straight lines. The following Table gives some of the results got with wires each one foot long :—

Best Value of a	Value of n	Value of b
140	·79	947
130	·76	765
120	·78	535
160	·74	783
150	·79	1035
180	·78	1242

TABLE OF HEATING EFFECT

Temperature	Value of a	Value of n
275° C.	100	·86
339	120	1·02
358	60	1·26
368	40	1·60
372	20	1·80
375	14	1·80 and 1·90
377	6 and 5	2·15 and 1·90
400	5 and 0	2·10 and 2·30
413	2	2·40 and 2·60
466	4	2·30 and 2·80
485	3 and 2	2·15 and 2·70
535	4	2·30 and 2·55
625	1 and 0	2·60 and 3·20
675	2	2·40 and 2·90

FIGURE 2—Showing relation of (n) and (a) with Temperature.



TIME EFFECT

In these temperature experiments, the plan adopted was to raise the brass wire up to the temperature indicated, and to remove it from the furnace at once, as it was found by previous tests that the change was a sudden one. Wires were introduced for $\frac{1}{2}$ hour, $\frac{1}{4}$ hour, 5 minutes, and 1 minute, respectively, at a temperature of 400° C., and in each case the same values of n got.

LOWERING OF TEMPERATURE

A length of original [1] wire was allowed to remain in liquid air for over half an hour and subsequently tested, but this seemed to have no effect upon the value of n; and this result

[1] This term will be used in subsequent pages to denote a length of wire cut from a coil as supplied by the dealer.

was also got on treating in the same manner a portion of wire already heated past 375° C.

Effect of Extensional Strain

A length of the original wire was hung with a 14-lb. weight attached in a long vertical shaft, and portions cut from it were tested at intervals of days or weeks, but no change was observed. The weight was then replaced by one of 28 lbs., and latterly of 56 lbs., but still the same values of n were observed. The wire after heating to 400° C., however, could be easily elongated by a pull; and on subsequent testing it was found to give results tending to approach those obtained with an unheated length of wire. A wire 12 inches in length was raised to 400° C. and then stretched till rupture occurred. The value of a was found to have changed to 100, whilst n was found to be 1·34, the points again all falling into one straight line. The diameter was now 0·90 mm., and the change of length 3 inches. Thus stretching is followed by a reversion to the original conditions of the unheated wire; and it is quite probable that, with more careful stretching, the value of n could be reduced to its original amount. The effects of repeated extensional and torsional strains on brass are treated subsequently.

Wires of Varying Diameter

It was found that a wire, of diameter 1·2 mms., gave results similar to those got for that of diameter 1·0 mm. The exact values got were

$$a=95,\ n=\cdot70,\ b=439.$$

A thicker wire, of diameter 1·65 mms., gave the results

$$a=85,\ n=\cdot66,\ b=360.$$

In this case the readings had to be taken very quickly, since the oscillations died down with extreme rapidity, and

thus the accuracy could not be so great as in the former experiments. This was found to be even more apparent in the next experiment, with a wire of diameter 2·0 mms. It was found impossible to take readings with any degree of accuracy with 12 inches of this wire, and so a double length was taken. Distinct pendulum oscillations were also of more frequent occurrence when the thick wire was used, and the curve obtained showed a wavy appearance. By drawing a straight line through the observed points, so as to eliminate the disturbing effect, the following results were obtained :—

$$a=90, \quad n=\cdot 84, \quad b=427.$$

This value of b, as shown on page 117, can be compared with the values got with the wires already discussed. For it was shown that in a wire of half length

$$b'=b\frac{1}{2^n}.$$

Thus the value of b will be got for that of double length by

$$b=b'\cdot 2^n$$
$$=238.$$

The value of b, then, although not exactly under control, is seen to decline steadily with increases of diameter, thus :—

Diameter	a	n	b
1 mm.	About 100	·70—·80	700—1000
1·2 mms.	95	·70	439
1·65 „	80	·66	360
2·0 „	90	·84	238

The values of a and n, then, are largely independent of change of sectional area, just as they were of change of length. This is to be expected, in accordance with the original assumption that the loss of energy for a given material depends solely on a power of the angle of distortion.

Annealing from High Temperatures

A length of brass wire heated to 535° C. was annealed and then tested. The values got,

$$a=1, \quad n=2{\cdot}30,$$
$$a=1, \quad n=2{\cdot}70,$$

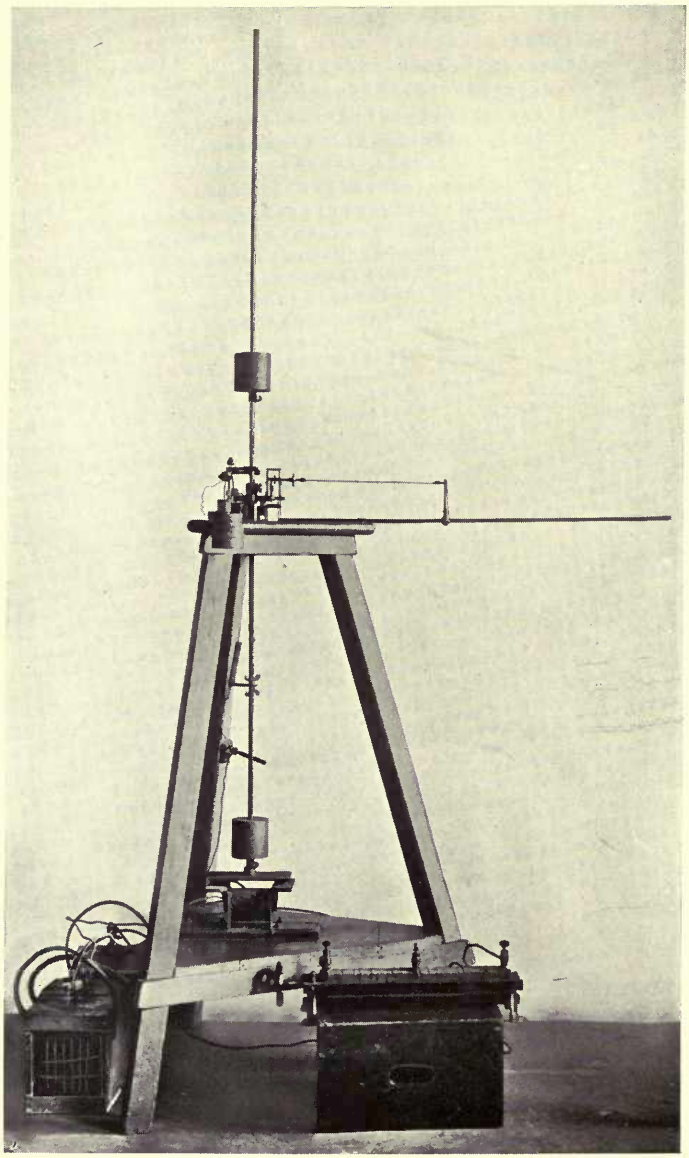
show no change from those for wire heated to 535° C., and quickly withdrawn from the furnace. On that occasion the values got were $a=4$, $n=2{\cdot}30$ and $2{\cdot}60$. An experiment when the wire was annealed from 485° C. also showed no change.

Results with various other Wires

Wire	Best value of a	Value of n	Effect of Heating
Aluminium	0 and 100 (two lines)	1·34 and ·20	Tendency of wire to assume form of one straight line.
Copper	0 and 15 (two lines)	3·80 and 1·60	No visible change.
German Silver	110	1·05	Still one line, values being $a=20$, $n=1{\cdot}70$.
Zinc	0	·60	.....
Silver	65	·45	.....
Tin	3	·82	.....
Platinum	28 and 30 (two lines)	·95 and 1·05	.....

THE EFFECTS OF FATIGUE ON TORSIONAL OSCILLATIONS

In the preceding observations it was noted that the application of a large extensional force had a great effect in some cases, notably in the case of several of the metals after having



been raised to a red heat in the electric furnace. The undernoted work was undertaken to find the effect produced by a repeated application of an extensional force and by a repeated application of a twist to one end of the wire, the other end being held firm, thus tending to induce fatigue in the wires, the supposition being that such treatment might have an effect on the mode of oscillation when tested immediately afterwards. The latter step is necessary, since it has been shown (Peddie, *Trans. Roy. Soc. Edin.*, vol. xxxix., 1897-1898) that rapid partial recovery from fatigue is possible.

The apparatus used for imparting these continued strains is a modification of an earlier machine used by Dr. Peddie in these investigations, and was designed by him, the cost of construction being defrayed by means of a Royal Society grant given for the purpose.

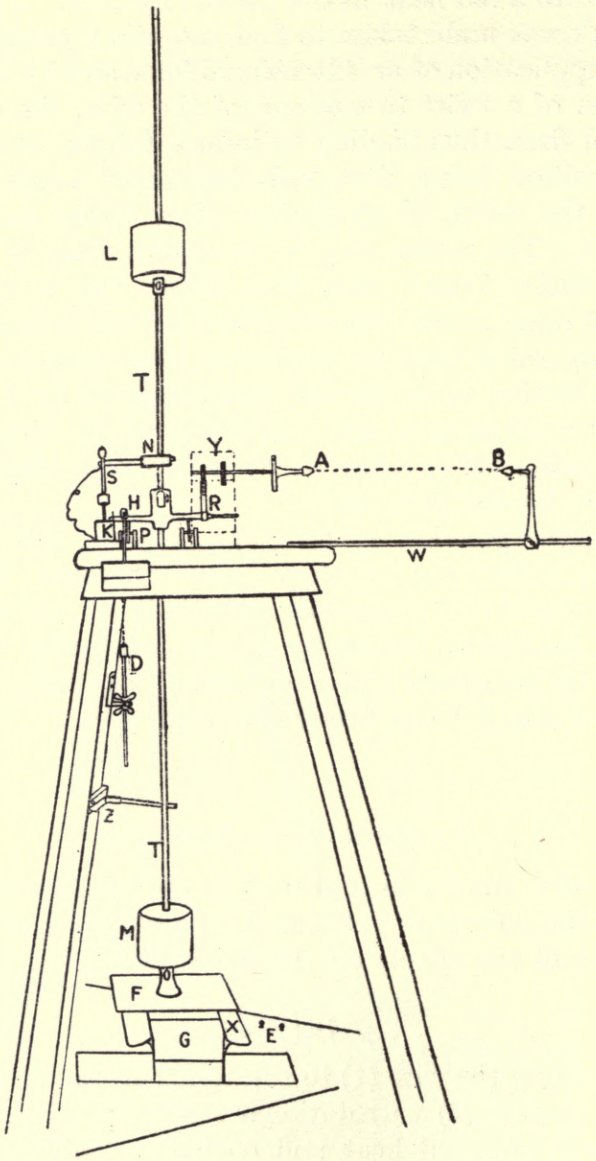
The accompanying photograph shows the complete apparatus, with the battery and rheostat introduced into the circuit. It consists essentially of an electrically oscillated pendulum, which by means of a series of toothed wheels at its mid-point twists one end of the wire introduced, the other end of it being firmly clamped.

Experimental Results

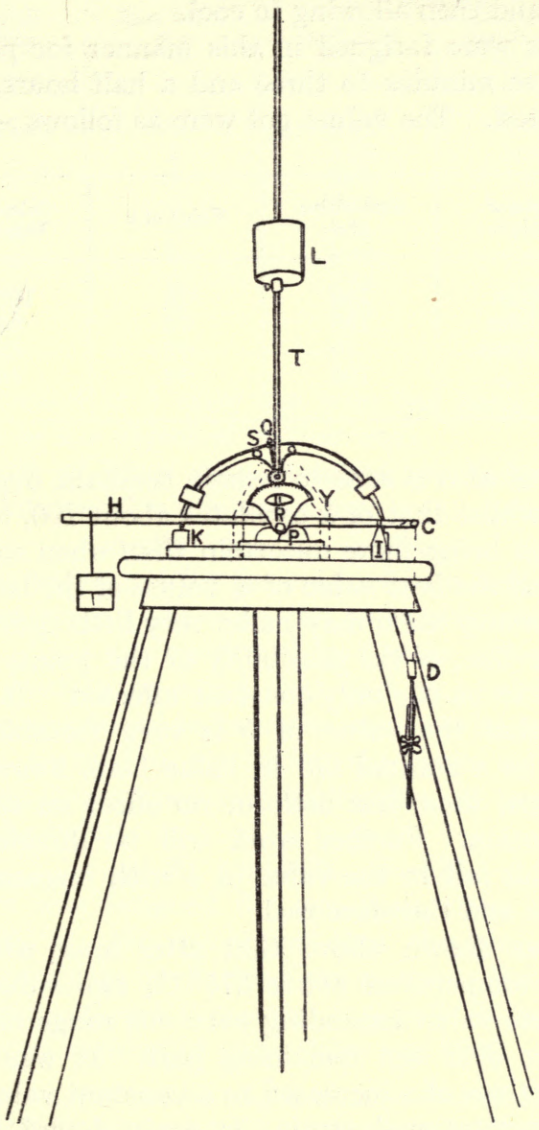
Brass wire, similar to that used in the temperature experiments, is the only wire yet tested, and experiments included the finding of the effects on the constants n, a, and b of the equation

$$y^n (x+a)=b$$

after subjecting the wire (1) to rotational strain in the original unheated state; (2) to rotational strain after the wire had been raised to a red heat and cooled, *i.e.* after the points obtained by plotting log $(x+a)$ against log y could not be fitted into one straight line; (3) to extensional strain in the



FRONT VIEW OF APPARATUS: *D—H*, WIRE FOR EXTENSIONAL STRAIN; *A—B*, WIRE FOR ROTATIONAL STRAIN



END VIEW OF APPARATUS: *D—C*, WIRE FOR EXTENSIONAL STRAIN

unheated state; and (4) to extensional strain after raising to a red heat and then allowing to cool.

1. Wires were fatigued in this manner for periods varying from five minutes to three and a half hours, and subsequently tested. The values got were as follows :—

Time of Fatigue	Best Value of a	Value of n	Calculated Value of b
5 mins.	100	·78	1000
1 hour	180	·78	834
$2\frac{1}{2}$ hours	70	·78	560
$3\frac{1}{2}$ „	100	·76	484

The value of n is seen to remain constant over this range of fatigue, whilst that of a oscillates about 100, the values of a when large being more uncertain than when small, since in trying to find the best value of a, values of the latter differing by ten or twenty units may make very little difference in the slope of the line, or the possibility of the points lying along it; b seems to be the only constant affected. It has already been seen that the value of b is very variable, but there *appears* to be a gradual fall in value here, however. Rotational fatigue, then, has little or no effect on the constants of the equation. Further work will be directed to ascertaining if this fall in the value of b with increase of fatigue is invariable and therefore real.

2. It was shown above that after brass wire had been raised to a temperature above 375° C., two values of n were obtained, one value extending over one range of oscillation, and another over the remaining part. It was shown also that these values of n increased to a constant value. Fatigue, induced by rotational strain, is again found to have no effect on the constants a and n, as the following results will show :—

Time of Fatigue	Best Value of a	Values of n	
		1st Part of Curve	2nd Part of Curve
0 mins.	0	2·52	3·00
5 „	2	2·50	3·20
10 „	1	2·51	3·10
15 „	0	2·53	3·02
30 „	0	2·81	3·00
60 „	0	3·36[1]	3·03
120 „	0	2·56	3·03
180 „	2	2·59	3·07

The behaviour of b after the wire has been heated and fatigued will be the object of further work.

3. A length of brass wire, clamped vertically between C and D, and fatigued for two and a half hours, gave the values

$$a=90, \quad n=\cdot 76, \quad b=841.$$

These are the values got for the original wire, and thus extensional fatigue has no effect on the constants when the wire is unheated. This was confirmed by further experiments.

4. After heating to a red heat and then cooling, extensional fatigue was found to have the same tendency as stretching had—*i.e.* to tend to straighten the curve so as to allow of one straight line representing the results. A typical experiment gave the values

$$a=30, \quad n=1\cdot 24, \quad b=524.$$

This wire was fatigued for one hour after having been raised to 485° C. It was found that the pendulum made twenty-five complete oscillations per minute ; therefore, since the wire between C and D receives two pulls during one oscillation, the total number of pulls given was 3000. The weight

[1] This value, 3·36, got for the line lying along the points of the first oscillations, is quite abnormal, and the wire used in this experiment was examined to discover, if possible, the cause of the unusual value of n. A repeated experiment gave the same result. The wire was then halved, each half being tested separately, and finally the abnormality was traced to one of the quarters.

attached to the end H of the lever was 3000 gms., and the ratio of the arms 3 to 1, the fulcrum I being half way between the cam P and the end C, while PH=PC. The pull exerted is therefore in this case 9000 gms. weight. The values got on testing this wire after heating to 485° C., and before fatigue was applied, were

$$a=2, \quad n=2{\cdot}15 \text{ and } 2{\cdot}70 ;$$

a then is seen to be raised to a value intermediate to those obtained from the fresh and heated wires. Similarly n has now an intermediate value.

The effects of both forms of fatigue on the empirical equation as applied to other materials will be the object of further research.

JAMES BONNYMAN RITCHIE

WAVE IMPACT ON ENGINEERING STRUCTURES

THE failure of a breakwater, formed of blocks of masonry or concrete, under wave impact, is usually initially due to undermining or settling of the foundations, or to the displacement of some one or more of the face blocks, this permitting free access to the interior of the mass. Once any such serious displacement has taken place, total failure is usually a matter of comparatively short time.

As is a well-known fact, the normal impact of a wave on the face or top of such a structure may produce the withdrawal of a block weighing several tons, the motion of the block being in the opposite direction to that of impact.

Thus at Ymuiden, a 'header' block in the seaward face of the pier, measuring 7 ft. in length and presenting a face to the waves of 4 ft. by 3 ft. 6 ins., was started forward to the extent of 3 ft. by the stroke of a wave *compressing the air behind it.*[1] This block weighed about seven tons, and the top of it was at the level of low water. It had three courses of concrete blocks, each 3 ft. 6 ins. in thickness, resting upon the top of it. These were all set in Portland cement mortar, but the course to which the block in question belonged was built dry, as were those below it. A similar instance was noticed at East London (Cape Colony) where several adjoining blocks were forced outwards on the harbour side of the breakwater during a storm.[2] Another example of this was noticed by

[1] This description is from Shield's *Principles and Practice of Harbour Construction*, p. 83. The italics, however, are the author's.

[2] Wm. Shield, *Harbour Construction*, p. 109.

Mr. Mallet on the sea-walls of the Dublin and Kingstown railway [1] during a severe gale, in which masses of water, deflected vertically upwards by the sea face of the wall, fell heavily upon the pavement inside. In this case many of the square granite pavement blocks were seen to jump vertically out of their beds at the instant of the fall of the sea upon them and were thrown landwards towards the line of way.

The commonly accepted explanations of such a phenomenon will be gathered from the following quotations from authorities on harbour works. Mr. Vernon Harcourt notes:—

'The blocks at and below low water have open joints, into which air penetrates on the recoil of a wave and also fills any cavities behind; and the succeeding wave, compressing the air inside, leads to the gradual forcing out of a block by the pressure from behind on the retreat of each wave during a storm.' [2] In another passage the same writer remarks, 'Waves striking against the outer blocks also compress the air in the open joints, which aids in the displacement of the inner blocks.' [3]

A somewhat similar but wider explanation is to the effect that, 'The air or water confined within a joint, when struck by a wave, is converted into a very destructive agent. The air is compressed and forced along joints and seams, and, immediately upon the wave receding it expands and tends to loosen and push out pieces of the rock. When water is confined in joints the force of the wave stroke is transmitted by it, and is made to act over large areas on the same principle as a hydraulic press.' [4]

Similar views were adopted by Captain D. D. Gaillard, U.S.A.,[5] who, as a result of experiments, came to the conclusion that the pressure due to the impact of an interrupted

[1] *Proc. Inst. C.E.*, vol. xviii. p. 113.

[2] Vernon Harcourt, *Civil Engineering applied to Construction*, p. 486.

[3] Vernon Harcourt, *Harbours and Docks*, p. 298.

[4] Wm. Shield, *Harbour Construction.*

[5] *Wave Action in Relation to Engineering Structures*, Capt. Gaillard, p. 181.

jet of water on a normal plane is no greater than that of a continuous jet of the same velocity; that waves therefore exert a continuous pressure over a definite period of time and not a sudden momentary blow, and that as a result of this continued pressure on a wall with open joints the wave forces water through the joints, and compresses the air in the interior. As the recession of a wave is sudden compared with its advance, the pressure is suddenly withdrawn from the outside, and the excess internal pressure results in outward displacement of the face blocks.

Experiments at Roorkee [1] on the impact of jets on a normal plane, also led their authors to the conclusion that the maximum pressure produced by sudden impact is the same as is exerted by a steady jet, and is given, within about 1 per cent., by 'H' or $v^2 \div 2g$ feet of water where 'H' is the effective head producing flow, measured above the point of impact. In these experiments the pressures were measured by a water-column, in communication with small orifices in the plane.

The present investigation has been carried out in the engineering department of University College, Dundee, with a view of determining the magnitude of the effects which such actions as have been outlined, may produce, and of showing that still another phenomenon may be called into play during wave impact, and may produce much greater effects than are compatible with these theories of simple hydrostatic transmission of pressure, or of air compression.

Pressure following impact—When a mass of water is hurled with velocity 'v' against the face of a breakwater, the pressure on the face rises almost instantaneously to a value approximating to $v^2 \div 2g$ feet of water. Substantial confirmation of this is afforded by the results of experiments by the late Thos. Stevenson, who, measuring these impact pressures by means of a dynamometer with spring control,[2] fixed at about

[1] *Proc. Inst. C.E.*, vol. lx. p. 436.

[2] *Trans. Roy. Soc. Edinburgh*, vol. xvi. p. 23.

the level of ¾ tide, obtained maximum values of 3½ and 3 tons per square foot at Dunbar and on the Banffshire coast. These values correspond to heads of 122 and 105 feet and to velocities of 89 and 82·3 feet per second respectively. This mass of water being diverted by the face of the breakwater will then be projected upwards to a height approximately the same as that corresponding to this pressure. As the result of observation it is known that on the breaking of a wave, during a storm, masses of water are, on occasion, hurled to heights in the neighbourhood of 150 feet, and even greater heights have been occasionally recorded.[1]

As, however, the breakwater causes an upward deflection of the air currents in such an onshore wind as commonly accompanies the production of large waves, this will probably account to some extent, for the extreme height to which the spray is often thrown, and there would appear to be some doubt as to whether, apart from this action, the height exceeds some 100 to 120 feet, except in very abnormal cases. Throughout the present paper calculations have been made on the assumption that this face pressure may attain a value of 6400 lbs. (2·86 tons) per sq. foot, corresponding to a head of 100 feet and to a velocity of 80 feet per second.

If water accumulates in the interior of a breakwater and is in communication with the sea-face through one or more crevices or open joints which are themselves full of water, such a face pressure may be transmitted hydrostatically to every portion of the interior. Moreover, as all portions of the face may not be exposed to direct wave impact at the same instant, this may give rise to an internal pressure tending to cause outward displacement of the blocks, which may thus attain an effective value of 6400 lbs. per square foot of projected area of the block.

Effect of air compression in the joints—Let the joint Fig. 1 *a*, have a length *l* feet, perpendicular to the sea-face,

[1] *Harbour Construction*, Shield, pp. 80 and 208.

and a cross-sectional area 'a' square feet. Let this communicate at its inner end directly with the surface of the enclosed water, and imagine a frictionless piston to form a definite boundary between the entrapped air and the impinging column of water. Let 'x' be the distance to which this column penetrates on its first impact.

If the column loses no energy during its entry to, and passage up, the joint, the energy given up by it when it has come to rest equals $62{\cdot}4ax\frac{v^2}{2g}$ foot lbs.[1]

Equating this to the work done on the air during compression, and assuming this, because of the rapidity with which it takes place, to be adiabatic we have

$$62{\cdot}4\frac{v^2}{2g}.ax=\frac{p_1(l-x)-p_a l}{{\cdot}4}\times a$$

where p_a is the initial atmospheric pressure (2120 lbs. per square foot) and p_1 is the final air pressure. Substituting for p_1 in terms of p_a we finally get

$$62{\cdot}4x.\frac{v^2}{2g}=\frac{2120l}{{\cdot}4}\left\{\left(\frac{l}{l-x}\right)^{\cdot4}-1\right\}$$

and if $\frac{v^2}{2g}=100$ this simplifies to

$$1{\cdot}18\frac{x}{l}+1=\left(\frac{l}{l-x}\right)^{\cdot4}.$$

The value of the ratio $x\div l$, which satisfies this equation is independent of l, and is equal to ·81, in which case

$$p_1=p_a\left(\frac{1}{{\cdot}19}\right)^{1{\cdot}4}=10{\cdot}25 \text{ atmospheres},$$

$$=21{,}700 \text{ lb. per square foot},$$

$$=9{\cdot}7 \text{ tons per square foot}.$$

[1] This assumes fresh water of weight 62·4 lbs. per cubic foot. As fresh water was used in the author's experiments this value has been adopted in these calculations. In the case of sea water the value would be $64ax\frac{v^2}{2g}$ foot lbs.

Actually the maximum pressure attained will be less than this, because energy is lost by eddy formation at the entrance to such a passage ($\cdot 5v^2 \div 2g$ if the edges are sharp and normal to the face) and by friction during motion up the passage, while it is probable that except in a joint of very small cross-sectional area the motion of the water will be rather of the type indicated in Fig. 1, *b*, than in Fig. 1, *a*. Such a type of motion, leading to backward displacement of the air over the top of the advancing column would produce further loss of energy in eddy formation. It appears probable that in no case could the loss of energy, due to these various causes, amount to less than 25 per cent. of the initial energy of impact, and that it would normally amount to 50 per cent. or even more. The effect of such losses on the maximum pressure obtainable in this way is shown in the following table :—

Initial head =100 feet Velocity =80. ft. per sec.	Percentage loss of head	0	25	50
	Max. pressure attained in tons per sq. ft.	9·7	4·9	2·13
	Ratio of max. pressure to pressure on face	3·49	1·77	·77

In any case, however, should the face pressure be maintained for a sufficient length of time, water will be forced along the crevice until the internal pressure is equal to the face pressure.

Experiments by the authors, the results of which are given at a later stage, showed that using a light piston to simulate the state of affairs, shown in Fig. 1, *a*, the maximum pressure attained by air compression was 2·48 times the face pressure, while without this piston it was 2·05 times the latter pressure. As the state of affairs in these experiments was particularly

suitable for the production of such pressures it is probably safe to say that in a sea-wall the maximum internal pressure due to air compression never exceeds twice the face pressure,

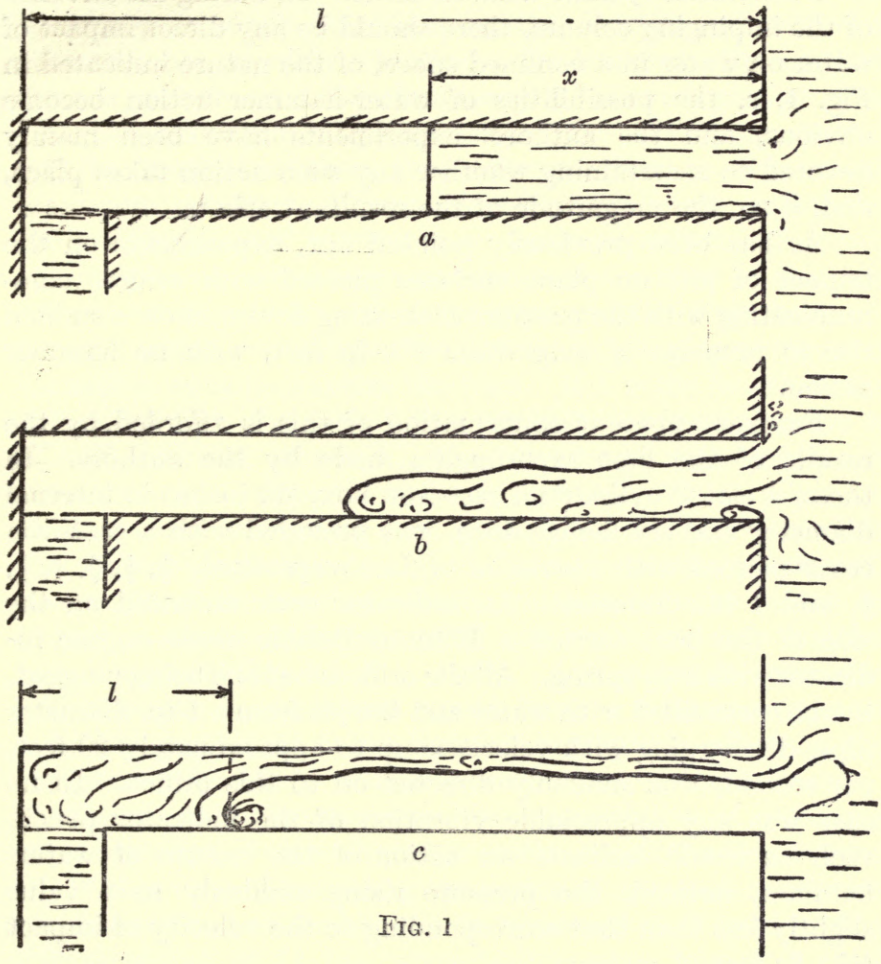


FIG. 1

i.e. does not exceed some 5·75 tons per square foot with a velocity corresponding to a head of 100 feet.

Where the crevice opens into a cavity of any considerable size in the interior of the-sea wall, or where, as will be usually

the case, the latter is sufficiently porous to allow of the escape of air under pressure, a further and indefinite reduction of pressure will follow.

Possibilities of water-hammer action—If, during the advance of the impinging column, there should be any direct impact of water on water in a confined space, of the nature indicated in Fig. 1, *c*, the possibilities of water-hammer action become obvious, and the authors' experiments have been mainly devoted to ascertaining whether any such action takes place, and, if so, the magnitude of the resultant effects.

As has been previously pointed out, experiments on the impact of jets on plane surfaces pierced with orifices communicating with the pressure-measuring device, show a sudden rise in pressure of magnitude $v^2 \div 2g$ feet, with no hammer action.

Further apparent confirmation of this is afforded by the results of the first experiments made by the authors. In these, a closed cylindrical cast-iron box, six inches in internal diameter and six inches deep, was provided with a cast-iron cover pierced with a series of orifices respectively $\frac{1}{8}$, $\frac{1}{4}$, $\frac{3}{8}$, $\frac{1}{2}$, $\frac{5}{8}$, $\frac{3}{4}$, and 1 in. diameter. An indicator cock mounted on the side of the box, carried a M'Innes Dobbie steam-engine indicator with a $\frac{1}{10}$ spring. All the orifices but one being plugged, the box was filled with water and the jet from a 1-in. diameter pipe, discharging with velocities up to approximately 20 feet, per second, was suddenly directed on to this orifice. In no case was any appreciable vibration of the indicator pencil, such as would indicate an action of the nature of water-hammer, noticed, the pressure rising suddenly to a value slightly less than that corresponding to the velocity of impact ($v^2 \div 2g$ feet of water).

A little consideration, however, shows that under circumstances such as obtained in these experiments and in those previously noted, the absence of any indication of water-hammer action by the pressure recorder does not necessarily

prove that such action does not occur. The indicator or water column adopted as a measuring device is a system capable of vibrating naturally with a frequency n per second. If to this system is applied a steady force, or a periodic force whose frequency is much less than n, the actual and recorded pressures are sensibly identical. If, however, the applied force is periodic, and if its frequency 'q' is much greater than 'n,' the maximum displacement of the indicating system will be much less than that corresponding to the actual maximum pressure. Where water-hammer is set up by the sudden stoppage of motion in an enclosed column of water, pressure waves alternately positive and negative in sign are reflected from end to end of the pipe and the disturbance is periodic with a period depending on the length of time required for such a wave to traverse the pipe. If L is the length of the column in feet, the period of a complete cycle of pressure is $4L \div V_p$ seconds, where V_p, the velocity of propogation of pressure waves through water is normally about 4700 f.s. It is evident that with such an apparatus as was used in the authors' experiments and in those previously mentioned, the length of the moving column which is brought to rest on impact is almost infinitely small and would be zero but for the compressibility of the water. Any pressure vibration which might be produced would have a frequency almost infinitely great, and could have no perceptible effect on the comparatively slowly vibrating mechanism of the indicator.

Under such circumstances, the impossibility of obtaining any indication of water-hammer action is sufficiently obvious.

With a view of increasing the period of any such oscillation of pressure and of enabling it to be recorded, if produced, a coil or zigzag of 1½ ins. wrought-iron pipe, having a total length of 100 feet (Fig. 2), was next built up. The upper end of this was open and the lower end was provided with a tee-piece carrying a steam-engine indicator, and terminated in a 1-inch valve V through which water could be admitted

to, or discharged from, the pipe. In the impact experiments the coil was filled through this valve up to the point ' *A*,' care being taken to displace all air. A jet of water from a $1\frac{1}{2}$-in hose was then suddenly deflected into the open end of the horizonta pipe ' *C*,' an indicator diagram being taken simultaneously at the lower end of the coil.

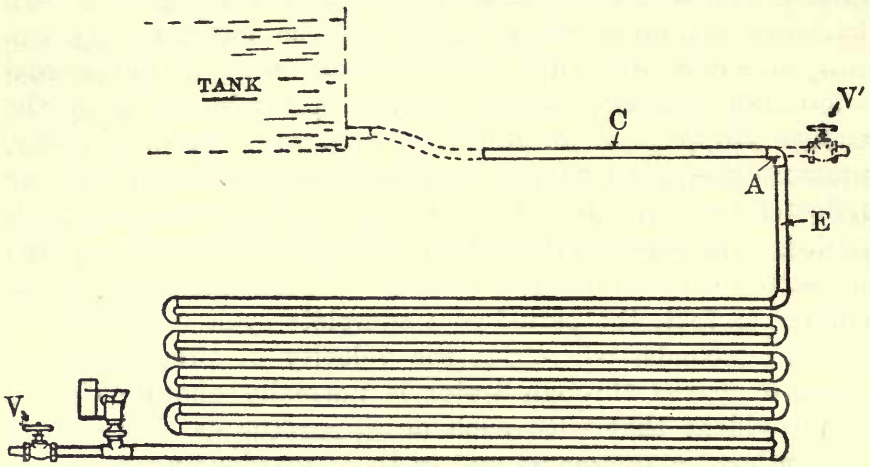


FIG. 2

The length of the horizontal pipe ' *C* ' was varied in these experiments from 5 inches to 70 inches. In some of the experiments with a view of ensuring that the phenomena should be due to air compression alone, the interior of this pipe was bored out to a smooth parallel surface and the jet was directed on to a light easily fitting piston placed immediately inside its open end. In other experiments, flow was allowed to take place through the valve towards the open end of the coil so as to keep the latter full of water, and impact took place on to the end of this moving column of water, thus simulating the state of affairs which exists during wave impact on a joint which is discharging water from a cavity under pressure. In other of the experiments the horizontal pipe was removed and the jet played vertically downwards

into the open end of the vertical pipe 'E,' this being either full or partially full of water, thus simulating the conditions under which a falling sea impinges on the pavement joints of a breakwater. The mean results of this work are given at a later stage of the paper.

Before studying the effect of jet impact on the coil, a series of experiments was carried out to determine the pressures to be obtained by definite water-hammer. For this purpose the open end of pipe 'C' was coupled up to a large tank, the level of whose free surface was 4·5 feet above the outlet valve V. Water was allowed to discharge through the coil under this head; the discharge was collected for a given time and weighed and the velocity of flow computed, and the rise in pressure behind the valve following a sudden closure of the valve was measured. If 'v' is the mean velocity of flow in feet per second, the rise in pressure following an instantaneous stoppage of flow in a rigid pipe line is given by $p=v\sqrt{\frac{KW}{g}}$ lbs. per square foot,[1] where 'K' is the bulk modulus of the water and 'w' is its weight per cubic foot. The mean temperature of the water was 45° F., at which temperature 'K'$=43\times10^6$ lbs. per square foot, and this value makes $p=9130\ v$ lbs. per square foot$=63{\cdot}4\ v$ lbs. per square inch. Actually the stretching of the pipe line and its distortion under pressure absorb an appreciable amount of energy and especially so when, as in the present case, the pipe line is not anchored in any way. A large number of experiments were carried out with varying velocities of flow, and, as shown in Fig. 3, on plotting, these are found to lie for some distance on a straight line, and to give the result $p=48\ v$ lbs. per square inch. Writing $p=\sqrt{\frac{K'W}{g}}$, where K' is the effective modulus as modified for pipe distortion this makes $K'=24{\cdot}6\times10^6$ lbs. per

[1] *Water Hammer in Hydraulic Pipe Lines*, Gibson, p. 39.

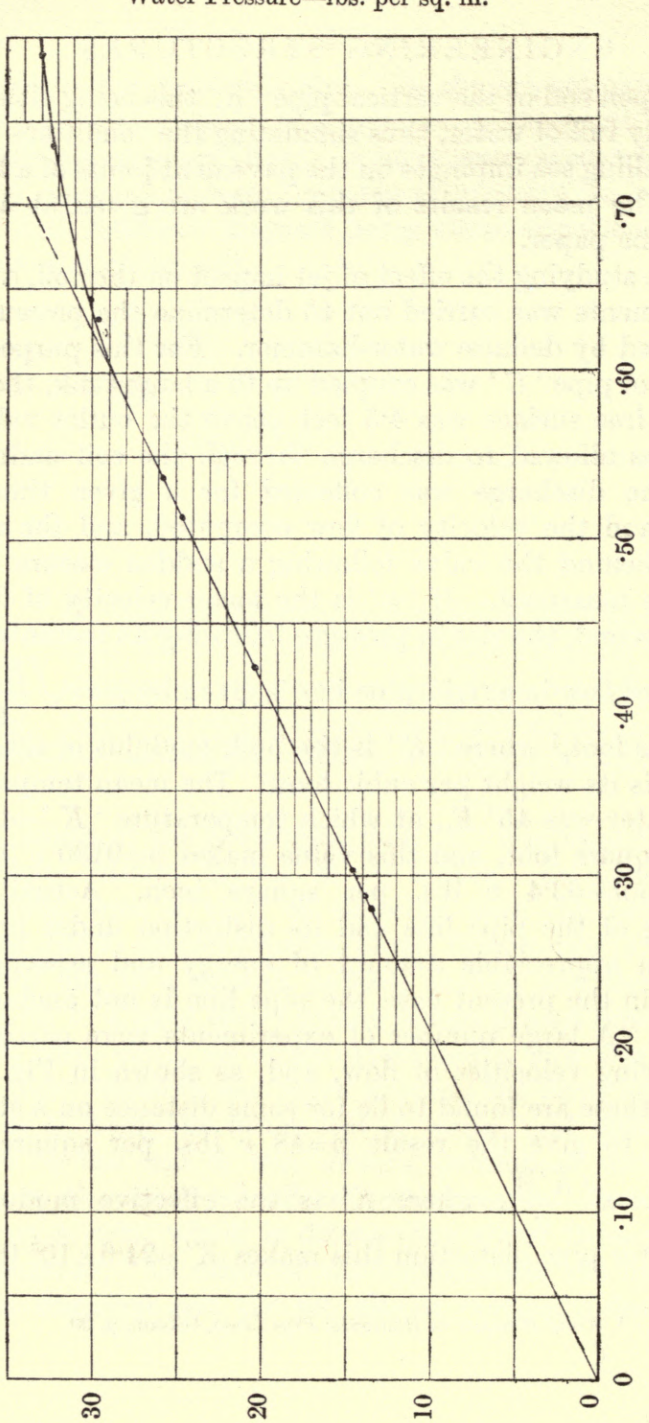

Water Pressure—lbs. per sq. in.
30
20
10
0
·0
·10
·20
·30
·40
·50
·60
·70
Velocities of flow—feet per second

FIG. 3

square foot,[1] and as the velocity of propagation of pressure waves through such a column of fluid is given very approximately by $V_p=\sqrt{\frac{K'g}{W}}$, this velocity, for the experimental pipe line, is 3400 feet per second.

Although valve closure was not instantaneous, it may readily be shown that if closure is complete before the disturbance produced reaches the open end of the pipe, *i.e.* if the time is less than $l \div V_p$ or $\frac{1}{34}$ second, the pressures produced are the same as would accompany instantaneous stoppage. The fact that up to a discharge of 25·7 lbs. per minute (v=·60 f.s.) the pressure is equal to 48 v lbs. per square inch for all velocities, shows that up to this point the time of closure was less than this, and indicates that for this discharge and corresponding valve opening, the time was approximately $\frac{1}{34}$ second.

Impact of a moving on a stationary column of water—When a column of water which is confined laterally, impinges on a stationary column of the same fluid, the magnitude of the hammer pressure may be shown to be one-half that attending sudden stoppage by means of a valve. On playing a jet into the open end of pipe '*C*' Fig. 2, except for the effect of the entrapped air a sudden rise in pressure, of magnitude 24 v lbs. per square inch, would be attained throughout both the moving and the stationary columns. This pressure is independent of the length of either of these columns. Assume, as will be commonly the case in a sea-wall, that the length of the stationary column of water filling a cavity which may extend for some considerable distance in the interior of the mass, is greater than that of the impinging column, which is largely governed by the length of the crevice piercing the face. As in the experimental coil, a mass of water hurled at the open end forms a column which will, except as modified by the

[1] *Water-Hammer, ante cit.*, p. 16.

presence of air, impinge on the end of the stationary column with velocity v. At the instant of impact let its length be l feet. Impact is followed by a rise in pressure at the junction of the columns, and a wave of compression (24 v lbs. per square inch above normal) is propagated in opposite directions from this point. The wave traversing the impinging column reaches its free end after a time, $l \div V_p$ seconds. At the same time the wave traversing the stationary column has also travelled a distance of l feet, and at this instant, that portion of the joint column nearest the open end of the pipe, and of a

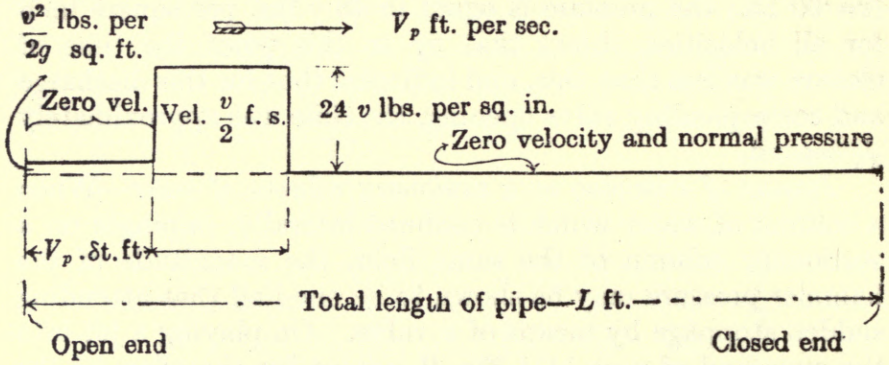


FIG. 4

length $2l$ is under an identical state of pressure and velocity, this pressure being 24 v lbs. per square inch above normal and the velocity $v \div 2$ towards the closed end. At the open end the stressed layers rebound outwards, the pressure falls to that obtaining at this point, *i.e.* to $h \div 62{\cdot}4$ lbs. per square foot, or to zero if the face pressure has been removed, and a wave of normal statical pressure and of zero velocity is propagated along the pipe in the rear of the pressure wave. The state of affairs after a further short interval of time δt is then as represented in Fig. 4.

When the front of the pressure wave reaches the closed

end of the pipe the motion is suddenly stopped and the pressure rises to $p=48\ v$ lbs. per square inch. After a further interval, $2l \div V_p$ seconds, that portion of the column, of length $2l$, nearest the closed end is at rest under this pressure, the rest of the pipe being under normal pressure and zero velocity. Instantaneously, however, the end of this stressed column, which is more remote from the closed end, rebounds with velocity $v \div 2$ and pressure $24\ v$ lbs. per square inch, layer after layer following suit, until after a further interval, $2l \div V_p$ seconds, this is moving under this state of pressure and velocity towards the open end. The dilatation, under this tendency to retrograde motion, of those layers in contact with the closed end, causes the pressure to fall to normal, and a state of normal pressure and of zero velocity is now reflected to the open end, following the preceding pressure-velocity wave, whose state occupies a length, $2l$, of the pipe at each instant. When this former wave reaches the open end the pressure falls to that obtaining at this point, the velocity increases to 'v,' and a wave of normal pressure and of velocity 'v' (towards this end) is reflected towards the closed end. On arriving at that portion of the pipe in which the pressure is normal and the velocity zero, the pressure becomes $-24\ v$ lbs. per square inch, and the velocity $v \div 2$ and a wave conveying this state over a length $2l \div V_p$ of the pipe, travels on towards the closed end. On its arrival the pressure becomes $-48\ v$ lbs. per square inch, the velocity zero, and this state is reflected to the open end again. Arriving here, the pressure becomes suddenly normal, the velocity becomes v towards the closed end, and the whole cycle is repeated. The true pressure-time diagrams, as obtained respectively at this end, and at a point l' from the end would then appear as in Fig. 5, *a* and *b*.

Since in a number of the jet experiments l', the distance of the indicator from the closed end of the pipe, was greater than $2l$, the theoretical pressure diagram at this point in such cases would be as indicated in Fig. 5, *c*, the maximum pressure at

this point in the pipe never exceeding 24 v. The diagram as recorded by the indicator will, however, in general show smaller maximum pressures than those actually obtained at this point, because of the extremely short interval of time during which these pressures are exerted. A close approximation

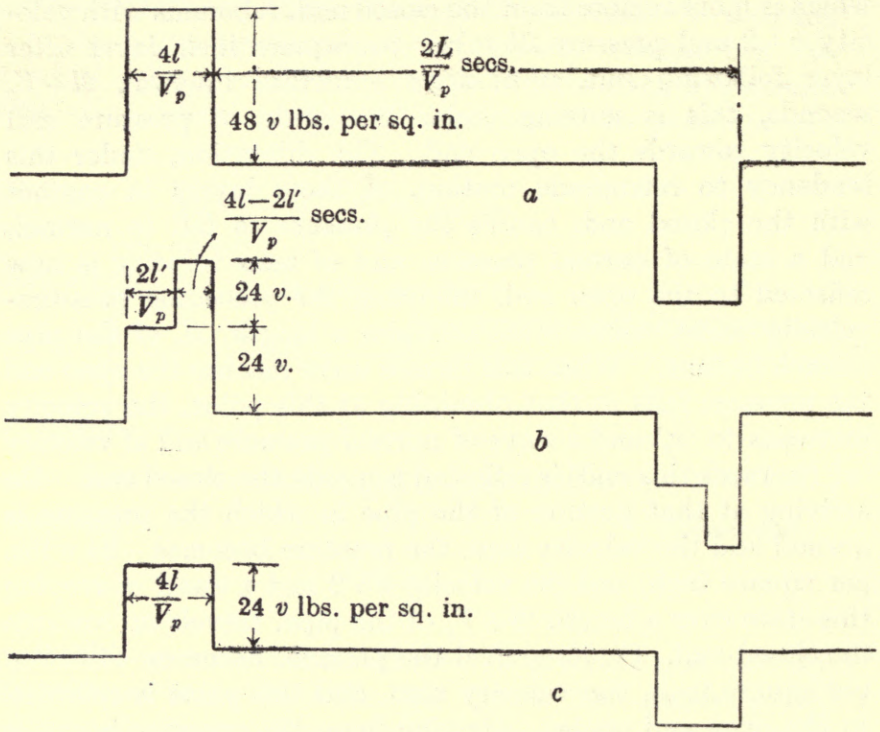


FIG. 5

to the effect of the suddenly applied force on the indicator may be got by assuming it to be uniform over the time $4l \div V_p$ seconds. Let F be the magnitude of the force on the piston in lbs.; let $\frac{W}{g}$ be the effective mass of the indicator piston line and linkage, and let 'S' be the stiffness of the

indicator spring, so that $\frac{F}{S}$ would be the displacement of the piston under a steady force F.

The equation of motion now becomes

$$\frac{W}{g} \cdot \frac{d^2x}{dt^2} + Sx = F$$

where 'x' is the displacement of the piston at time 't' seconds after the first application of the force F, and the solution of this is

$$x = \frac{F}{S}\left\{1 - \cos\sqrt{\frac{gS}{W}} \cdot t\right\} \text{ft.}$$

This shows, that if the time 't,' during which the force F is applied, is very short, the recorded pressure is less than the true pressure at the indicator in the ratio $1-\cos\sqrt{\frac{gS}{W}} \cdot t$, where $t = 4l \div V_p$ seconds. The value of the term $\sqrt{g\frac{S}{W}}$ can be obtained, experimentally, since the frequency of the natural vibration of the indicator is equal to $\frac{1}{2\pi}\sqrt{g\frac{S}{W}} = n$. Values of '$n$' were obtained by mounting the indicator on the cylinder of a gas engine, taking a diagram, and counting the number of oscillations traced out during a definite portion of a revolution. The results of these observations were very consistent and gave the following results:—

Spring	$\frac{1}{60}$	$\frac{1}{40}$	$\frac{1}{10}$
n	250	204	102

The validity of this reasoning was checked by a series of experiments on the pipe line modified as shown by the dotted

lines in Fig. 2. Water was allowed to flow from an open tank through the upper horizontal length l of the pipe, through the valve V'. This valve being closed suddenly the corresponding hammer pressure was measured by the indicator at the lower end of the coil. The results of these experiments were very satisfactory, the pressures as calculated from the formula $p=48\,v$ lbs. per square inch, and as obtained from the indicator diagrams with ordinates multiplied by the corresponding multiplying factor, agreeing, for values of l between 20 inches and 60 inches, within about 3 per cent. Evidently if $l=0$, corresponding to normal impact on a joint which is full of water the value of the multiplying factor becomes infinitely great, and the indicator could only show the effect of a hammer pressure if this were also infinitely great.

A further check was obtained by taking diagrams under similar conditions with $\frac{1}{10}$ and $\frac{1}{40}$ indicator springs. Since n for the $\frac{1}{40}$ spring is twice as great as for the $\frac{1}{10}$ spring, the pressures indicated with the former spring for values of l in the neighbourhood of 25 inches ($\cos\sqrt{\frac{gS}{W}}\,.\,t=0$ for $\frac{1}{10}$ spring, $=-1$ for $\frac{1}{40}$ spring) should, if the reasoning is valid, be approximately twice those recorded with the weaker spring. The results showed that the pressures recorded by the stronger spring were higher in a ratio which varied from 1·75 to 2·2.

Adopting the formula as giving substantially accurate results, it becomes possible to deduce, from an indicator diagram, the true pressures in the pipe when a jet is suddenly diverted into its open end, provided only that water-hammer actually does take place.

A preliminary series of experiments, carried out to settle this point, showed that by slightly modifying the method of application of the jet, two distinct types of diagram could be obtained. The jet played instantaneously and normally on to the open end, usually gave a diagram identical with those obtained when the piston was in use (Fig. 6 *a*) indicating that

the phenomenon was due to air compression alone. If more gradually applied, so as to facilitate displacement of air by the incoming water, a very different state of affairs was indicated. Fig. 6, *b*, shows a diagram obtained under such

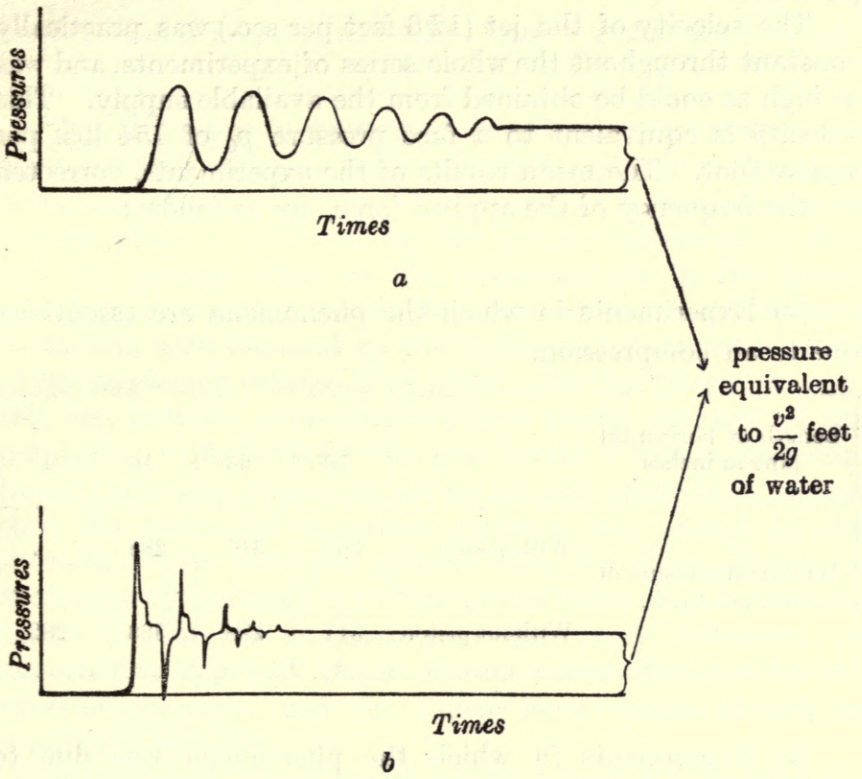


FIG. 6

circumstances. The initial rise in pressure is no longer gradual but is as instantaneous as that accompanying a sudden valve closure, and this is followed by rapid negative and positive alternations of pressure, substantially of the form indicated by theory, on the assumption of hammer action. The experi-

ments showed conclusively that under favourable circumstances water-hammer is set up by wave impact on an open joint, and experiments were then carried out to determine the magnitude of the pressures obtained in the experimental pipe line.

The velocity of the jet (12·6 feet per sec.) was practically constant throughout the whole series of experiments, and was as high as could be obtained from the available supply. This velocity is equivalent to a face pressure p_0 of 154 lbs. per square foot. The mean results of the experiments, corrected for the frequency of the applied force, are as follow :—

(*a*) Experiments in which the phenomena are essentially due to air compression.

Length of horizontal pipe in inches		70	65	16	4
Maximum pressure in lbs. per sq. ft.	With piston	367	310	288	..
	Without piston	317	288	388	282

(*b*) Experiments in which the phenomena was due to water-hammer.

(1) Jet played into horizontal pipe.

Length of horizontal pipe in inches	70	65	56	16	4
Max. pressure, lbs. per sq. ft.	504	632	763	1450	3040

(2) Jet played into vertical pipe.

Length of empty portion of vertical pipe in inches	23	14	8	2	1
Max. pressure in lbs. per sq. ft.	1220	2160	2340	11000	14400

The diminution in the magnitude of the maximum pressures given in these tables, as the length of the passage is increased, is undoubtedly due partly to the reduction in the velocity of impact which is produced by the greater resistance to flow and the greater effect of the entrapped air in the longer passages, and partly to the fact that while the multiplying factor has been deduced on the assumption that the length l of the impinging column is identical with that of the passage, this can only be approximately true in the shortest of the passages. Unfortunately the true length l cannot be ascertained with any degree of accuracy, and while it is certain that the maximum pressures attained are, except in the shortest of the passages, greater than are given above, no very close approximation to their actual value can be obtained. Under favourable circumstances they may, however, be expected to approach the maximum values obtained for the shortest passages, and for safety such values should be considered possible.

It is evident, moreover, that with values of l less than the least of those experimented upon, the effect of the entrapped air would become increasingly small, and the results appear to show that with an infinitely small value of l the pressure would ultimately approximate to the value corresponding to sudden stoppage of a column moving with the velocity of impact. In these experiments this would be 87,500 lbs. per square foot, or approximately six times the pressure obtained when l is 1 inch.

In certain of the experiments an air valve, $\frac{1}{4}$ inch diameter, was mounted at the upper side of the horizontal pipe at its inner extremity, and was left open during impact. Where the diagrams showed the phenomenon to be due to air compression, the effect of this in reducing the maximum pressures was very marked. Where water-hammer occurred the effect was very erratic, the maximum pressures being in some cases as high as, and in other cases much lower than, when the valve was closed.

The question as to how far the results may be considered to apply in the case of wave impact on a sea-wall, is of some interest. Probably the average sea-wall will be comparable, as regards rigidity, with the experimental pipe line, and, except as regards porosity, pressures of the same order of magnitude may be anticipated with the same velocity of wave impact. Any such porosity will, however, considerably reduce the maximum pressures obtained, whether due to water-hammer or to air compression, while the presence of any cavity forming an air chamber at the inner end of any open joint will effectively prevent hammer action. Still, since the magnitude of the hammer pressures are directly proportional to the velocity of impact of water surface on water surface, and since this is probably approximately proportional to the velocity of wave impact in all cases, it is evident that with velocities in the neighbourhood of 80 feet per sec. (6·3 times those obtaining in these experiments), internal pressures of the order of 40 tons per square foot may, under favourable circumstances, be developed. Fortunately each application of such a pressure only lasts for an almost infinitely small interval of time, and the shorter the effective length of the joint, and the less in consequence the modifying effect of the entrapped air and the greater the pressures attained, the less is the time over which the pressure is exerted. Still, even so, its effect, in gradually breaking down the adhesion of block to block, is likely to be extremely serious.

Conclusions—The main conclusions to be drawn from the investigations are that while, on the assumption of simple hydrostatic transmission of pressure, the effective internal pressure due to wave impact cannot exceed that exerted by wave impact on the sea face of a breakwater, the pressures produced, if the energy of the wave is devoted to compression of air in the open joints, may amount to approximately twice this magnitude. If, however, conditions are favourable to the production of water-hammer, considerably greater pressures, up to some fifteen times the face pressure with very high velocities of impact, are to be regarded as possible.

The results suggest the desirability of providing a free outlet for such water as may percolate to the interior of a sea-wall or breakwater, by means of a series of weep holes or drains opening on its sheltered face. Such drains, preventing the accumulation of internal water, would be an effective guard against the production of internal pressures of sufficient magnitude to affect the stability of the structure, whether due to water-hammer or to air compression.

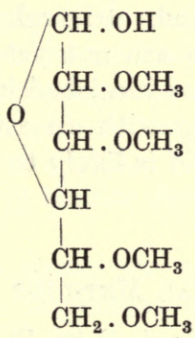
ARNOLD HARTLEY GIBSON
WILLIAM NELSON ELGOOD

CHEMISTRY

THE PREPARATION OF PARTIALLY METHYLATED SUGARS AND POLYHYDRIC ALCOHOLS

MUCH of the work which has appeared from the Chemical Research Laboratory of St. Andrews during the past ten years has been concerned with the preparation and properties of methylated sugars in which only the reducing group remains unsubstituted. As examples of such compounds we have the tetramethyl derivatives of glucose, fructose, mannose, and galactose, trimethyl arabinose and trimethyl rhamnose. The study of alkylated sugars of this nature has yielded results of theoretical interest which are referred to in detail in another communication to this volume.[1]

It will be seen, however, by inspection of the formula of a typical example, such as tetramethyl glucose:



that the reactivity of the molecule is practically confined to

[1] Young, *A General Review of Purdie's Reaction.*

one position—the unmethylated reducing group. Considering that methylation increases the stability of a sugar and also confers a greater range of solubility on the product, it is evident that partially methylated derivatives of the sugar group would be compounds possessing a special interest. The characteristic properties of the parent sugar would be more closely preserved than in the case of a fully substituted compound, a richer variety of reactions would be available, and, at the same time, the more obscure decompositions undergone by sugars in virtue of the high hydroxyl content of the molecule, would, to a large extent, be precluded.

As examples of the many possible applications of such compounds we have: (1) their use in testing the various theories of alcoholic fermentation; (2) their capacity to be converted into mixed ethers of sugars or polyhydric alcohols, compounds which possess a special interest for the physiologist; (3) the accumulation of optical data showing the effect of successive substitution in the sugar group, and (4) the opportunity afforded by the study of the mode of formation of these compounds for obtaining experimental evidence of configuration.

Several examples of definite mono-, di-, and trimethylated hexoses have been prepared by workers in St. Andrews during the past three years, and, although the different lines of research indicated above are not yet completely developed, the work already done has furnished interesting results which are now submitted, along with an estimate of the direction which research in this field is likely to take.

Experimental Methods Employed

The general method devised by Purdie and Irvine for the preparation of fully methylated sugars does not permit of

the isolation of incompletely substituted derivatives other than compounds of the nature of trimethyl glucose. In the first paper of the series, however, the authors pointed out that, in order to protect a sugar from oxidation during the silver oxide reaction, all that is necessary is to substitute the reducing group by a condensed residue capable of subsequent removal by hydrolysis. For obvious reasons, derivatives of the nature of methylglucoside have been largely made use of for this purpose, but other types of sugar derivatives may also be employed. Of these, the compounds produced by the condensation of sugars with ketones or aldehydes are best adapted for the purpose required. For example, a glucosidic monoacetone derivative of a hexose must, irrespective of the linkage of the acetone residue, contain three hydroxyl groups capable of methylation, so that hydrolysis of the alkylated product should give a trimethyl hexose ; similar treatment of a diacetone derivative would result in a monomethylated aldose or ketose. The remaining type of a partially alkylated hexose would be represented by a dimethyl glucose, and this has now been prepared by alkylation of monobenzylidene methylglucoside, and removal of benzaldehyde and methyl alcohol by hydrolysis.

The principles sketched above have been found to be capable of general application, and it is possible, by the introduction of hydrolysable residues into the sugar molecule, to protect selected hydroxyl groups from alkylation, so that the preparation of a large number of partially methylated sugars is thus rendered available. The process is also applicable to the preparation of similar derivatives from polyhydric alcohols.

The following table shows the methods adopted in the formation of the more important compounds of this class which have so far been obtained :—

Condensed Sugar Derivative.	No. of Methoxyl Groups introduced.	Groups removed by Hydrolysis.	Methylated Sugar Derivative.
Glucosediacetone . .	1	Two mols. acetone	Monomethyl glucose
Benzylidene-α-methyl-glucoside	2	Methyl alcohol and benzaldehyde	Dimethyl glucose
Glucosemonoacetone .	3	One mol. acetone	Trimethyl glucose
Fructosediacetone . .	1	Two mols. acetone	Monomethyl fructose
Rhamnosemonoacetone	2	One mol. acetone	Dimethyl rhamnose
Mannitol monoacetone	4	One mol. acetone	Tetramethyl mannitol
Mannitol diacetone .	2	Two mols. acetone	Dimethyl mannitol
Glycerol monoacetone	1	One mol. acetone	Monomethyl glycerol

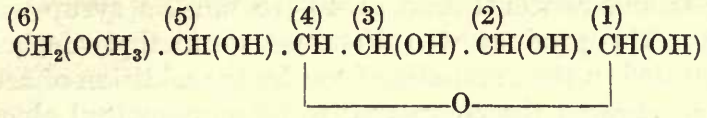
MONOMETHYLATED REDUCING SUGARS

It has hitherto proved impossible to obtain definite monosubstituted sugars other than the glucosides or metallic derivatives. As the compounds now described are reducing sugars they are thus examples of a new class.

Monomethyl Glucose

The constitution assigned to this compound will be discussed later, and it will be shown that the methoxyl group is

attached to the terminal carbon atom in the sugar chain, *i.e.* in the position marked No. 6 in the following formula :—



The substance may therefore be termed 6-monomethylglucose.

The method of preparation adopted was to condense glucose with acetone under conditions which result in the formation of glucosediacetone (Fischer, *Ber.*, 28, 1165, 2496). The reaction is troublesome and uncertain in its results, on account of the necessity to convert glucose in the first instance into a dimethyl acetal, and, moreover, as the acetone residues are exceedingly liable to undergo hydrolysis, precautions have to be taken throughout the preparation to avoid the access of either moisture or traces of acid. We have, however, been able to improve on Fischer's process, and have succeeded in increasing the yield of product considerably. The methylation of the substance was conducted with the precautions found advisable in the case of the corresponding fructose derivative, and the same proportion of the alkylating mixture was used. The product was purified by fractional distillation (b.p. 139-140°/12 mm.) and the yield was almost quantitative.

Analysis showed the compound to be pure monomethyl glucosediacetone, the properties and solubilities of which resembled those of other methylated sugar derivatives of a glucosidic nature.

The compound showed $[\alpha]_D^{20°} -32{\cdot}2°$ in alcohol and $-31{\cdot}8°$ in acetone solution, the concentration in each case being 5 per cent.

The removal of the acetone residues took place with extreme ease on heating an aqueous-alcoholic solution, containing 0·4 per cent. of hydrogen chloride, for 100 minutes in boiling water. The course of the reaction was followed polarimentrically, and the results showed that both acetone groups were

removed simultaneously and apparently at the same rate. After neutralisation with silver carbonate, shaking with animal charcoal and concentration at 40°/15 mm., a syrup was obtained. The product was dissolved in methyl alcohol and precipitated in the crystalline form by the addition of acetone. Analysis showed the compound to be monomethyl glucose in a state of purity. The substance shows all the characteristic properties of a reducing sugar, melts sharply at 157-158° and is more soluble in organic solvents than the parent glucose. When crystallised as described the compound showed mutarotation:

$c=2{\cdot}46$, Solvent=methyl alcohol. $[\alpha]_D^{20°}+98{\cdot}6° \longrightarrow 68{\cdot}0°$.

This form is accordingly regarded as the α-isomeride.

The β-form of the sugar has also been isolated by the method subsequently described under dimethyl glucose. This form showed the upward mutarotation $+28° \longrightarrow +68°$, and the optical values are thus in fair agreement with those calculated by the method recently described by Hudson.

The position of the methyl group in monomethyl glucose was readily established as, on treatment with phenyl hydrazine and acetic acid, the sugar gave a monomethyl glucosazone identical with that previously obtained from monomethyl fructose. In the case of the latter sugar, direct experimental evidence exists which indicates that the methoxyl group is terminal.

Monomethyl Fructose

No detailed account of the isolation of monomethyl fructose need be given here, as a description of the compound is included in Mr. Young's contribution to this volume. The method adopted was substantially the same as that followed

in the preparation of the corresponding glucose compound, and thus included the intermediate formation of monomethyl fructosediacetone. This compound crystallises in square plates melting at 115°, showed $[\alpha]_D - 136{\cdot}4°$ in methyl alcoholic solution, and was hydrolysed by heating with 0·1 per cent. hydrogen chloride. The rotatory changes then observed indicate that the two acetone residues are removed in successive stages, an observation which is of importance in establishing the constitution of the compound. The subsequent isolation of the free sugar was carried out in the usual manner and yielded monomethyl fructose as a readily crystallisable sugar melting at 122-123° and showing all the properties of a reducing ketose.

The following observations of mutarotation were made :

Solvent.	Initial $[\alpha]_D$ of α-form.		Permanent $[\alpha]_D$.		Initial $[\alpha]_D$ after fusion.
Water . . .	−70·5°	⟶	−53·1°	⟵	−41·9°
Methyl Alcohol	−74·1°	⟶	−22·1°	⟵	−12·5°

The constitution of the sugar, deduced from its behaviour towards phenyl hydrazine, oxidising agents, and in condensation reactions, is represented by the structure :

$$CH_2(OCH_3).\underset{|__________}{CH}.CH(OH).CH(OH).\underset{__________|}{C(OH)}.CH_2(OH)$$

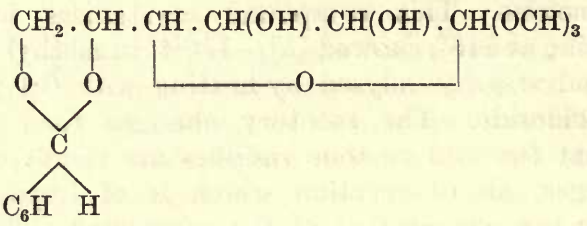
(the CH and C(OH) groups being joined through O)

DIMETHYLATED REDUCING SUGARS

Dimethyl Glucose

For the preparation of this compound two of the hydroxyl groups in glucose, in addition to the reducing group, must be protected from methylation by the introduction of hydrolysable residues, and we thus made use of the benzylidene α-methylglucoside described by Van Eckenstein.

It will afterwards be shown that the most probable structure for the latter compound is that given below :



According to this view of the constitution a new asymmetric carbon atom is introduced into the molecule, and thus benzaldehyde should condense with α-methylglucoside so as to produce two isomeric products. This possibility seems to have been overlooked by Van Eckenstein, but we have succeeded in isolating the hitherto unknown isomeride by cautious crystallisation of the accumulated mother liquors obtained in a large scale preparation of the condensation compound. The new stereoisomeride crystallises in short prisms melting at 148-149° and shows $[\alpha]_D^{20°}+96{\cdot}0°$ in aqueous solution. This compound, which is only produced in small amount, is therefore *d*-benzylidene-α-methyl-*d*-glucoside.

The methylation of *l*-benzylidene-α-methylglucoside proceeded with unusual smoothness as, although acetone was required to promote the solution of the compound in methyl iodide, one treatment with the alkylating mixture was sufficient to effect complete methylation. The product was readily obtained in the crystalline state in nearly quantitative amount, and, after recrystallisation from ligroin, melted at 122-123°. The specific rotation in acetone solution for $c=1{\cdot}64$ was $+97{\cdot}03°$. It was found possible, by heating the compound for one hour at 95° with one per cent. hydrochloric acid, to remove the aromatic residue without affecting the glucosidic group. The product of this reaction was therefore dimethyl α-methylglucoside, which was isolated in the usual manner. The compound, when crystallised from hot benzene,

melted at 80-82° and behaved as a glucoside towards Fehling's solution. The specific rotation in aqueous solution was +142·6° a value which is practically identical with that found for a solution in acetone.

When boiled for 30 minutes with 10 per cent. hydrochloric acid, the glucosidic group was removed, and, on working up the product, dimethyl glucose was obtained in the form of a syrup which gradually crystallised on standing. After crystallisation from ethyl acetate, the sugar was obtained in the form of well-developed prisms which gave satisfactory analytical figures but which melted very indefinitely. This behaviour was shown to be due to the presence of the stereoisomeric α- and β-forms, both of which were ultimately separated.

When the crystallisation from ethyl acetate is carried out with solutions containing not more than five per cent. of the solute, the sugar separates in clusters of delicate pointed prisms. This is the pure β-form (m.p. 108-110°) and thus shows upward mutarotation when dissolved.

Solvent.	c.	Change in Specific Rotation.		
Water . . .	5·00	+10·6°	→	+64·4°
Alcohol . . .	5·02	5·7°	→	49·4°
Acetone . . .	3·84	6·5°	→	50·9°

The compound showed the phenomenon of suspended mutarotation in acetone solution, and it was thus possible to obtain an exact record of the whole range of the optical change in this solvent.

The α-form of the sugar separates, along with the β-isomeride, from solutions in ethyl acetate containing from 5 to 10 per cent. of the solute. Separation of the two varieties was, however, effected by cautious precipitation from the equilibrium solution in alcohol by the gradual addition of ether. The first crops to separate consisted as before of the β-form, but from the mother liquors the α-isomeride (m.p. 85-87°) was

deposited in warty aggregates of microscopic prisms. These showed the reverse mutarotation in acetone solution.

Initial Specific Rotation.		Permanent Specific Rotation.
+81·9°	⟶	+48·3°

Dimethyl glucose is thus well adapted for the study of mutarotation in that both stereoisomeric forms are available, and the ready solubility of the sugar in solvents in which the change is slow permits of the initial values being exactly determined. The optical study of the compound is now complete, but the results obtained are beyond the scope of this paper.

Dimethyl Rhamnose

[Purdie and Young (*Trans.*, 1906, **89**, 1196).]

The preparation of this compound resembled that just described, but differed in one essential, in that only two hydroxyl groups in rhamnose require to be protected from methylation. This was effected by the use of Fischer's rhamnosemonoacetone. The properties of dimethyl rhamnosemonoacetone, and of the alkylated sugar obtained from it by hydrolysis, were normal, but the detailed study of the substituted rhamnose was restricted by the fact that it could not be obtained in the crystalline state. It was however shown for the first time, in the investigation to which reference is made above, that the condensation of acetone with reducing sugars involves two hydroxyl groups in the latter compounds. This result is naturally of special importance in devising methods for preparing partially methylated sugars.

TRIMETHYLATED GLUCOSES

2 : 3 : 5 Trimethyl Glucose [1]

Up to the present, three isomeric trimethyl glucoses have been prepared. One of these is the dimethyl methylglucoside already described : the remaining two compounds are reducing sugars which differ in the distribution of the methoxyl groups.

It has already been shown by Purdie and Irvine that the methylation of methyl glucoside gives trimethyl methylglucoside as the main product when the reaction is carried out in methyl alcoholic solution. Considering the mode of preparation of this compound and the reactions of the trimethyl glucose obtained from it on hydrolysis, it is evident that the primary alcoholic group present in the parent glucoside escapes methylation when the reaction is carried out in presence of excess of alcohol. In solubility, reducing power, optical activity, and general chemical character, including its oxidation to a lactone, trimethyl glucose resembles tetramethyl glucose closely. Substitution of methoxyl for hydroxyl in the three positions specified has therefore little effect on the properties of glucose, and this result is important as it will be afterwards shown that a change in the position of the alkyloxy-groups results in the complete alteration of the optical relationships.

No doubt the method just described is capable of general application as a means of obtaining trimethylated aldoses containing an unsubstituted primary hydroxyl group, but the risk of the product being contaminated with other derivatives, and the experimental difficulties encountered in purifying viscous syrups by vacuum distillation, have not induced us to extend the method to other examples.

[1] This nomenclature for derivatives of sugars, although not yet adopted in standard works of reference, seems specially advisable for the compounds described in this paper. Inspection of the formula for monomethyl glucose will indicate the carbon atoms to which the numbers refer.—J. C. I.

3:5:6 Trimethyl Glucose

$CH_2(OCH_3) . CH(OCH_3) . CH . CH(OCH_3) . CH(OH) . CH(OH)$

O

In the preparation of the above compound glucosemonoacetone was alkylated, first in acetone solution and afterwards in methyl iodide solution. The liquid product, isolated from the reaction, boiled at 138-139°/12 mm. and had apparently undergone partial hydrolysis as it possessed a decided action upon Fehling's solution, and gave, on analysis, figures intermediate between those required for trimethyl glucosemonoacetone and trimethyl glucose. This result is not surprising considering the ease with which glucosemonoacetone is hydrolysed. The optical values observed for the methylated acetone compound have in consequence little significance, but the fact that the compound is laevo-rotatory ($[\alpha]_D^{20°} - 27{\cdot}2°$ in methyl alcohol) is nevertheless remarkable.

The hydrolysis was carried out exactly as in the preparation of monomethyl glucose, but as the sugar could not be obtained in the crystalline state the syrup examined would consist of the equilibrium mixture of α- and β-forms. The proportion of the latter variety was therefore increased by heating the compound at 70° for half an hour, and, on solution in alcohol, the following optical values were obtained :—

Initial Specific Rotation.		Permanent Specific Rotation.
$-6{\cdot}2°$	$\longrightarrow$	$-8{\cdot}3°$

As already indicated, the rotatory power of this sugar is in every respect abnormal. Whereas both the α- and β-forms of glucose, and also of all the other known methylated glucoses, are dextrorotatory, the equilibrium value for 3 : 5 : 6 : trimethyl glucose is laevo. Not only so, but the mutarotation recorded above indicates that the β-form is either dextro- or feebly laevo-rotatory, as the change $\beta \longrightarrow \alpha$ results in an increase

of laevo-rotation. This is at variance with all other optical values obtained for the glucoses and admits of no simple explanation. The abnormality can hardly be due to a highly pronounced laevo-rotatory effect attending methylation of the primary alcohol group in the sugar chain, as inspection of the available optical data will show.

Applications of Partially Methylated Sugars

The various applications of these compounds have already been briefly referred to in the introduction, and it will be seen that they afford considerable scope for investigation. An additional question of theoretical interest was raised in the course of the work, this being the varying capacity of members of the sugar group to enter into condensation with aldehydes or ketones. Thus methylmannoside gives both mono- and dibenzylidene derivatives, while methylglucoside and methylgalactoside only condense with one molecule of benzaldehyde. Several other examples are known in which, although the necessary hydroxyl groups are present in a sugar derivative, and are moreover situated in the spatial proximity apparently favourable to condensation, are nevertheless incapable of participating in condensation reactions.

This behaviour seems to be due to the stereochemical arrangement of the hydroxyl groups, and consideration of the available data points to the idea that condensation proceeds readily when the reacting hydroxyl groups are in the *cis* position with reference to the internal ring of the sugar molecule, but not when they are in the *trans* position. These considerations permit of the configuration of the α- and β-forms of reducing sugars being definitely established, and obviously the study of partially methylated sugars will prove useful in developing this line of research, as compounds of this nature may be obtained in which only the *trans* positions in the molecule are methylated.

Again, in view of their convenient solubilities and the tendency of partially methylated sugars to display suspended mutarotation, it is evident that these compounds are suitable substances for the study of the rotatory powers of α- and β-forms and of the rotatory changes shown in the formation of equilibrium mixtures, as it is possible to obtain an accurate polarimetric record of the tautomeric changes without calculation of the true initial values. In this way we have shown that both monomethyl and dimethyl glucose conform to the generalisation established recently by C. S. Hudson regarding rotatory power in the sugar group. The general question of the optical effect of methylation on the rotatory powers of glucose has also been studied in the course of the work. The results will shortly be published, but the discussion is beyond the scope of this paper.

With regard to the application of the new compounds in testing the theories of alcoholic fermentation it is evident that the use of monomethyl glucose offers special advantages. The current theories are chiefly based on the analogy of other reactions of sugars, and can thus be tested by the isolation of the intermediate products of the change. Although research in this direction has been highly profitable, the results obtained are in many cases conflicting or even contradictory. It will, however, be seen that, using monomethyl glucose as a substrate, the destiny of the methyl group at once gives a clue to the mechanism of alcoholic fermentation, as the position of the alkyloxy group in the molecule is known. Thus, according to Baeyer's dehydration theory, the fermentation products should be (1) methyl alcohol, (2) ethyl alcohol, (3) lactic acid, and (4) carbon dioxide. Wohl's theory, on the other hand, admits of a greater number of possibilities, but the most feasible should result in the formation of n-propyl alcohol, ethyl alcohol, α-hydroxybutyric acid, and carbon dioxide.

Similarly the dimethyl glucose now described should give either (1) dimethyl ether and ethyl alcohol, or (2) methyl

alcohol and *n*-propyl alcohol as the essential fermentation products.

As the more fully alkylated sugars are not fermentable, work of this nature could not be extended beyond the limits specified.

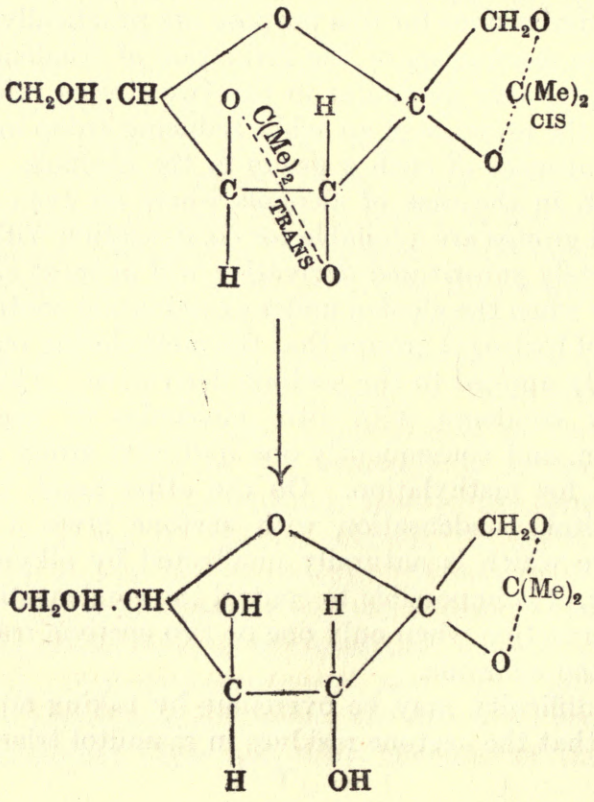
PARTIAL ALKYLATION OF POLYHYDRIC ALCOHOLS

Generally speaking, the same principles are utilised in the preparation of partially methylated polyhydric alcohols as apply to the formation of the corresponding substituted sugars, *i.e.* the methylation of a derivative which still contains hydroxyl groups, and the removal of the substituting residue by hydrolysis.

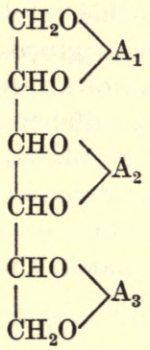
In the case of the alcohols most closely related to the sugars, suitable derivatives for this purpose are practically unknown, in fact the mechanism of the formation of condensation products is probably dissimilar in the two classes referred to, in virtue of the presence of an acidic reducing group in the sugars and the absence of such a group in the alcohols. It will be seen that, in the case of alcohols where an even number of hydroxyl groups are available for condensation with a ketone, a completely substituted derivative will in most cases result. It is only when the alcohol under examination contains an odd number of hydroxyl groups that the methylating reaction may be directly applied to the acetone derivative. Thus, arabitol can only condense with two molecules of acetone as a maximum, and consequently one hydroxyl group is thus left available for methylation. On the other hand, in the case of mannitol, condensation with acetone gives a triacetone derivative which is naturally unaffected by alkylation, and, moreover, it is impossible to control the condensation so as to stop the reaction when only one or two acetone residues have entered the molecule.

This difficulty may be overcome by taking advantage of the fact that the acetone residues in mannitol triacetone may

be removed in definite steps. This behaviour is doubtless controlled by causes similar to those which influence the partial hydrolysis of α-fructose-diacetone. Irvine and Garrett have shown that in the formation of this compound the addition of the non-glucosidic acetone residue involves torsion of the internal ring of the sugar molecule, but that the glucosidic acetone group is differently linked and occasions less molecular strain. The expressions *trans* and *cis* may be used to distinguish between the two types of linkage, and it has also been shown that carefully regulated hydrolysis removes the more unstable *trans* group, and thus a glucosidic monoacetone derivative remains. These considerations are illustrated in the formulae shown below :—



Before developing the argument further, it may be mentioned that the above speculations assume the ketonic residues to be attached so as to form five-membered rings. So far there is no rigid proof of this, but the results obtained in the study of the fructose-acetones are most easily explained on this assumption. Further, if we accept Fischer's view that ketones condense with β rather than with α carbon atoms a series of contradictions arises. Thus the arrangement is impossible in the case of glucosediacetone, and similarly the ketonic residues in mannitol triacetone cannot be arranged in accordance with this idea, as at least one pair of α carbon atoms must participate in the condensation. The simpler view is that this type of condensation is symmetrical, wherever possible, so that mannitol triacetone becomes :



If A_1, A_2, A_3 represent the acetone residues, it is seen that, considering the configuration of mannitol, A_2 must of necessity be a *trans* grouping, applying this expression in the sense already indicated. On the other hand, A_1 and A_3 may be either *cis* or *trans*. It does not necessarily follow that in each of these cases the more stable *cis* linking will result, as the relative positions of the terminal hydroxyl groups may conceivably be affected by the configuration of the remaining asymmetric systems, and they may thus react preferentially in one or other of the two alternative positions. Our results are in fact in agreement with this view.

Presumably then a difference in stability is to be expected in the three acetone residues in mannitol triacetone in virtue of the different effect of *cis* and *trans* grouping on the molecular balance. A further difference in stability might also be expected to arise from the fact that one acetone residue (A_2) substitutes the hydrogen atoms of two secondary hydroxyl groups, while the linkage of the remaining ketonic residues (A_1 and A_3) involves one primary alcohol group in each case. This factor, although no doubt present, does not seem to exercise any marked effect on the stability of the different groups as glucose diacetone, a compound in which the same conditions prevail, undergoes hydrolysis in one stage only. This at once points to the fact that the stability of the acetone residues is controlled by their stereochemical arrangement.

It is of course inadmissible to claim that results obtained with ring structures such as glucose and fructose must find exact analogies in the case of an open chain compound such as mannitol, but a close parallel has nevertheless been established in that carefully regulated hydrolysis of mannitol triacetone removes the ketonic residues simultaneously but at different rates. It is thus possible to isolate the intermediate compounds indicated in the following scheme:—

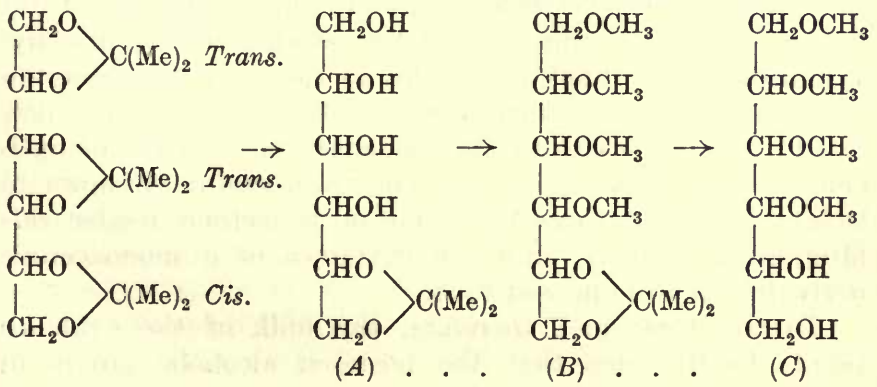
Mannitol triacetone → mannitol diacetone →
mannitol monoacetone → mannitol.

The reaction is naturally a troublesome one to control, but was effected by heating a 2·5 per cent. solution of the triacetone compound in 70 per cent. alcohol, containing 0·1 per cent. of hydrogen chloride, to 40° for about three hours. A continuous polarimetric record of the optical changes gave figures which, when plotted in a curve, showed two indefinite maxima followed by a regular fall to a constant value. On stopping the reaction at intermediate stages, it was found that, in the neighbourhood of the first maximum, the main product was a *mannitol diacetone* mixed with varying amounts of mannitol

and unhydrolysed material. Similarly, when the reaction was arrested at a time corresponding to the second maximum on the curve, the product was essentially *mannitol monoacetone.*

The formation of a definite mannitol diacetone, as the first step in the production of the monoacetone derivative, is obviously of great importance in tracing the course of this interesting hydrolysis, as it eliminates the possibility of the hydrolytic change being confined, in the first instance, to the acetone residues coupled in the primary alcoholic positions. Moreover, it indicates that there is a difference in the stability with which the terminal residues A_1 and A_3 are attached to the molecule, although the general symmetry of the structure would not justify this conclusion except on the assumption that there is a difference in the linkage of the groups (A_1 and A_3). The study of mannitol monoacetone lends support to this view. Methylation of the compound by the silver oxide reaction resulted in the formation of *tetramethyl mannitol monoacetone*, from which *tetramethyl mannitol* was obtained on hydrolysis. The fact that this compound may be oxidised by Fenton's reagent to give an alkylated reducing aldose, shows that the stable acetone residue was originally attached to a terminal primary alcohol group.

This series of reactions may therefore be interpreted in the following way :—



(*A*) Mannitol monoacetone :—
Crystallises in prisms melting at 85°.
Specific rotation in alcohol +26·4° (c=2·7).

(*B*) Tetramethyl mannitol monoacetone :—
Liquid boiling at 137-140°/11 mm.
Specific rotation in alcohol +39·0° (c=2·8).

(*C*) Tetramethyl mannitol :—
Liquid boiling at 167-169°/13 mm.
Obtained crystalline on standing.
Specific rotation in alcohol −12·5°.

The experimental evidence bearing on the constitution of mannitol diacetone is in the meantime somewhat incomplete. Alkylation of the compound gave *dimethyl mannitol diacetone* (b.p. 140-141°/13 mm.), and, on hydrolysis, a crystalline *dimethyl mannitol* was obtained (m.p. 93°; $[\alpha]_D$−8·8° in alcohol). The position of the methyl groups in the latter compound has not yet been determined, but there can be little doubt that they occupy positions 3 and 4 in the carbon chain. Inspection of the above results will show that the behaviour of mannitol triacetone on hydrolysis may also be explained to some extent by the assumption that the compound exists in two, hitherto unrecognised, isomeric forms, the arrangement of the substituent groups A_1, A_2, and A_3 being respectively *cis*, *trans*, *cis*, and *trans*, *trans*, *cis*. Until further work has been done on the constitution of dimethyl mannitol, it is perhaps premature to speculate too freely on the validity of this assumption, which certainly adds a new feature of complexity to the condensation reactions of optically active compounds, but our unsuccessful attempts to isolate a second form of mannitol triacetone render this alternative unlikely, and the existence of a monoacetone derivative is also opposed to it.

In the meantime, therefore, the bulk of the evidence points to the idea that the terminal alcoholic groups in

mannitol, although unconnected with an asymmetric carbon atom, assume preferentially different positions which affect the stability of the condensation derivatives. According to this view, mannitol triacetone exists in only one form, the linkage of the ketonic residues being *trans, trans, cis.*

Applications of Partially Methylated Polyhydric Alcohols

The most important application of these compounds will doubtless be found in the opportunity they afford for confirming configuration. From their mode of formation, the compounds contain hydroxyl and methoxyl groups, the position of the former alone being favourable to condensation with acetone. In other words, these groups represent *cis* and *trans* positions respectively in the original compound so that determination, by standard methods, of the distribution of the alkyloxy groups gives the configuration.

Another possible development of this line of research is the preparation of methylated aldoses, isomeric with alkylated sugars prepared from glucosides, but containing the methoxyl group in the γ-position and thus capable of functioning as aldehydes only. The examination of compounds of this class, with respect to their capacity to display mutarotation and to participate in glucoside formation, should afford definite evidence as to the structural causes of these phenomena in the reducing sugars.

Again, as in the case of partially methylated sugars, the behaviour of the corresponding alcohols towards catalytic fermenting agents should be capable of yielding results bearing directly on the mechanism of these changes.

Finally, the compounds are readily converted into mixed

ethers. Thus, ethylation of tetramethylmannitol results in the formation of a *diethyl-tetramethyl-mannitol*, and a *tetraethyl-dimethyl-mannitol* has also been prepared from dimethyl-mannitol.

Mixed ethers of this type are now receiving attention in view of their powerful narcotic properties, and, as the methods available for their preparation are not numerous and are of limited application, several processes for their production have recently been protected (D.R.P., 226454). By the process now described it should be possible to prepare mixed ethers of considerable complexity such as dimethyl-diethyl-dipropyl hexitols, in which the relative positions of the three types of alkyloxy groups could be varied, according to the order in which the alkylations were effected.

Although several workers have contributed the experimental data necessary for this paper, special acknowledgement is due to Mr. J. P. Scott, M.A., B.Sc. (Carnegie Fellow), who investigated the partially methylated glucoses now described for the first time. The section of the paper dealing with ethers of polyhydric alcohols is based on results obtained by Miss B. M. Paterson, B.Sc. (Carnegie Scholar).

It should also be stated that all necessary references to original papers on the alkylation of the sugars will be found in the bibliography appended to Mr. Young's contribution to this volume.

JAMES COLQUHOUN IRVINE

A GENERAL REVIEW OF PURDIE'S REACTION: ALKYLATION BY MEANS OF DRY SILVER OXIDE AND ALKYL IODIDES

Introductory Note

The process of alkylation by means of silver oxide and alkyl iodides was first employed by Purdie and Pitkeathly in 1899 (1).[1]

Prior to that time the original work which had appeared from the St. Andrews Chemical Laboratory had been concerned chiefly with the preparation, resolution, and examination of active acids and their derivatives. Several racemic alkyloxy-acids had already been obtained and resolved into their active forms. It was realised that these substances were of much importance, since their activity was found to be considerably greater than that of the parent hydroxy-compounds, and further, they were free from the disturbing effect on optical activity which is exercised by the hydroxyl group. The discovery of the 'silver oxide reaction,' as it may be called, rendered possible the direct conversion of esters of active hydroxy-acids into active esters of alkyloxy-acids, and thus greatly facilitated the work in hand. The application of the process to the synthetical introduction of alkyl groups has been extended in various other directions, which are indicated in this paper.

In the course of the preparation of ethereal salts by the

[1] The figures in brackets are the reference numbers to the original papers, the titles of which are arranged in chronological order in the bibliography appended to this communication. The abbreviations used are those adopted by the Chemical Society of London.

action of alkyl iodides on silver salts of hydroxy-acids, certain anomalous results were obtained. The ethereal tartrates prepared in this way, for instance, displayed abnormally high rotations, and it was ascertained that alkyloxy-derivatives were produced during the reaction. In endeavouring to obtain evidence of the production of these alkyloxy-derivatives, Purdie and Pitkeathly (1) found that the reaction between silver malate and isobutyl iodide gave rise to very little ethereal salt but to free malic and isobutoxy-succinic acids, and further, that isopropyl isopropoxysuccinate was formed during the interaction of isopropyl iodide and silver tartrate. Consideration of these results led to further experiments. Ethyl malate, ethyl iodide, and litharge, when heated together, showed no interaction, but on substituting mercuric oxide for litharge, a product which was more active than ethyl malate was obtained. Finally, when silver oxide was added to a solution of ethyl malate in isopropyl iodide, a vigorous reaction was found to ensue. A closer study of the reaction was now made; the materials used were ethyl malate, ethyl iodide, and silver oxide in the proportions calculated on the assumption that the reaction proceeds according to the following equation:—

$$OH \cdot C_2H_3(COOEt)_2 + 2EtI + Ag_2O = OEt \cdot C_2H_3(COOEt)_2 + EtOH + 2AgI.$$

From the reaction mixture pure ethyl *l*-ethoxysuccinate was isolated and its optical activity was found to agree with that of the ester prepared from the active acid previously obtained by resolution of the racemic acid (*Trans.*, 1895, 67, 972). The value of the reaction was further exemplified by ethylating ethyl tartrate by treating it with silver oxide and ethyl iodide in a similar manner; the product of the reaction was ethyl *d*-diethoxysuccinate. All previous attempts to alkylate the alcoholic hydroxyl groups of tartaric acid had been unsuccessful. It is thus seen that the discovery

of this method of alkylation was not a chance result, but was due to a careful and systematic tracing of an effect to its cause.

The reaction was immediately utilised for the preparation of the methyl methoxy- and ethyl ethoxy-propionates (Purdie and Irvine (2)), and the optical activity of the corresponding acids and their salts was determined and compared with the values obtained for the same compounds which had previously been prepared by resolution of the racemic acids by morphine (Purdie and Lander, *Trans.*, 1898, 73, 862). The comparison indicated that the alkylation process proceeded without any racemisation occurring. At the same time McKenzie (3) was able to prepare inactive and active phenylalkyloxyacetic acids by the alkylation of *i*- and *l*-mandelic acids and their esters.

In the following year (1900) Lander (4) published the results of an elaborate investigation of the general applicability of this method of alkylation. He was able to show that, by treatment with silver oxide and alkyl iodides, it is possible to substitute alkyl groups for the hydrogen in the hydroxyl groups of compounds of such widely different types as *l*-menthol, *i*-benzoin, ethyl acetoacetate and salicylic acid. The reaction of benzaldehyde with silver oxide and ethyl iodide leads to the oxidation of the substance and subsequent esterification of the resultant acid, ethyl benzoate being obtained. It was further shown that silver oxide and alkyl iodides react with amides and substituted amides, a hydrogen atom being replaced by an alkyl group. Acetanilide, for instance, yielded N-phenylacetiminoethyl ether $C_6H_5.N:C(OC_2H_5).CH_3$. The production of imino-ethers is therefore much facilitated by this reaction, since the preparation and isolation of the intermediate silver compounds are obviated.

The results which have been mentioned rendered it evident that the use of dry silver oxide and alkyl iodides constituted

a general means of synthesising alkyl derivatives of compounds of more or less well-defined acid character, possessing hydrogen atoms replaceable by alkyl radicles.

Advantages of the Process

There are many advantages attending the use of this method of alkylation. The products are generally obtained pure, in good yield, and there is no difficulty in separating the inorganic by-products. If an alkyl iodide has been employed in the alkylation, these by-products are silver iodide and water. The latter can in some cases be removed by employing a sufficient excess of the alkylating materials; in any case the insolubility of water in alkyl halides renders it of little effect on the course of the main reaction if no extraneous solvent is being used. The insolubility and stability of the remaining inorganic by-product, silver iodide, obviate any difficulty in the extraction of the organic product. The reaction is generally smooth and rapid in its course, and it can be very readily controlled. Alkyl iodides are, for the purpose of this reaction, more conveniently used than other halides. This is, possibly, simply a manifestation of the well-known fact that the elimination of silver iodide in organic synthesis occurs with great readiness. It is further possible that the iodides are more suitable than other halides by reason of their inferior stability. Alkylation proceeds most readily in the case of those compounds which are soluble in alkyl iodides, and in such cases no further addition of a solvent is necessary. It should be noted that the reaction is carried out in a neutral medium, and is therefore advantageously employed in the etherification of substances which readily undergo hydrolysis.

A further advantage of this method of alkylation is that it can be applied to optically active compounds without the occurrence of racemisation or inversion. In fact, up to the

present time, the reaction has been almost exclusively employed in the preparation of derivatives of active compounds, and in no case has an optical change of the nature of the Walden inversion been noticed. Purdie and Barbour (9) definitely proved that no inversion of this kind occurred on methylating methyl *d*-tartrate, as on hydrolising the methyl dimethoxysuccinate produced they obtained a dimethoxysuccinic acid, which, when reduced with hydriodic acid, gave *d*-tartaric acid. The proof has been extended by Irvine (33) to the methyl *l*-methoxy-propionate obtained by the methylation of methyl *l*-lactate. The substance was reduced with hydriodic acid and yielded *l*-lactic acid, which was identified by conversion into its zinc salt. The silver oxide method of alkylation has therefore no disturbing effect on the configuration of an active lactate. In some few cases (McKenzie (3)) racemisation has been observed, but it is not certain whether this occurred during the actual reaction or in the isolation of the product.

A modification of the reaction has been devised by Forster (44 and 45) for the purpose of esterifying acids without risk of racemisation. Silver oxide, in slight excess of the calculated amount, was mixed with an ethereal solution of *l*-α-triazopropionic acid, and, without separating the silver salt from the unchanged oxide, excess of ethyl iodide was added and left in contact with the mixture for thirty-six hours. The filtered solution yielded the desired ethyl *l*-α-triazopropionate $CH_3.CHN_3.CO_2C_2H_5$. Ethyl *l*-α-triazobutyrate was prepared in a similar manner.

By the action of silver oxide and methyl iodide on salicylic acid, Lander (4) obtained pure methyl *o*-methoxybenzoate. Similarly McKenzie (3) prepared *i*-ethyl phenylethoxyacetate from *i*-mandelic acid, and Denham converted glyceric acid into methyl αβ-dimethoxypropionate (private communication). We have here instances of esterification of the acids and alkylation of alcoholic hydroxyl groups proceeding

simultaneously, and from these results it would appear that the method might prove to be useful for the esterification of acids which give unstable silver salts.

The possibility of utilising the reaction as a means of determining constitution and configuration will be discussed later.

Range of Application of the Reaction

It may at once be stated that all stable compounds containing primary or secondary alcoholic hydroxyl groups or carboxyl groups invariably give positive results with the reaction if the compounds are soluble in the alkyl iodides or other neutral solvent; no cases have yet been encountered in which substances of the nature described have escaped alkylation by this process. Tertiary alcoholic groups, excluding those formed in tautomeric compounds by the keto-enol change, appear to entirely resist the action of the alkylating mixture. Lander (4) found, for instance, that triphenyl carbinol showed no change either when boiled for twelve hours with silver oxide and ethyl or isopropyl iodides, or even when heated with silver oxide and ethyl iodide in a sealed tube at 160° C. for four hours. The point is well illustrated by the experience of McKenzie and Wren (53), who subjected *i*-triphenylethylene glycol to two alkylations with silver oxide and methyl iodide, and obtained a monomethyl ether as the sole product. This product they proved to be β-hydroxy-α-methoxy-$\alpha\beta\beta$-triphenylethane $C_6H_5.CH(OCH_3).C(OH).(C_6H_5)_2$ and not the isomeric α-hydroxy-β-methoxy-$\alpha\beta\beta$-triphenylethane, since they obtained a substance identical with this product by the action of magnesium phenyl bromide on either *i*-benzoin methyl ether or *i*-methyl phenylmethoxyacetate. It is clear, therefore, that only the secondary alcoholic hydroxyl group of triphenylethylene glycol is methylated by the alkylating mixture; the tertiary hydroxyl group remains unattacked despite the excess of alkylating

materials used. A further instance was noted by Purdie and the writer (58), who found that the two hydroxyl groups of $\gamma\delta$-dimethoxy-$\beta\epsilon$-dimethylhexane-$\beta\epsilon$-diol $HO.C(CH_3)_2.CH(OCH_3).CH(OCH_3).C(CH_3)_2.OH$ resisted alkylation by this method.

As regards phenolic hydroxyl groups data are lacking, since experiments do not appear to have been made on the simple phenols. With certain substituted phenols, however, alkylation of the phenolic group occurred readily. Thus Irvine (5 and 11) prepared salicylaldehyde methyl ether in 90 per cent. yield by the action of silver oxide and methyl iodide on salicylaldehyde. Practically no oxidation of the aldehyde occurred, since only a trace of methyl *o*-methoxybenzoate was found in the product. Similarly Lander (4) prepared the latter ester directly from salicylic acid. The phenolic ethers so obtained were free from resinous matter, such as is generally produced during the preparation of these substances by the aid of alkyl iodides and caustic potash. On the other hand, Meldola and Kuntzer (52) obtained a negative result with a substituted phenol.

Although the silver oxide reaction finds its chief application in the alkylation of hydroxyl groups, yet, as Lander has shown (4, 6, 7, 13, 21, and 24), it is possible by its aid to substitute alkyl radicles for hydrogen in the molecules of amides and substituted amides. In this way imino-ethers may be prepared. An account of the results which have been obtained in this direction is given later.

Methods of Applying the Reaction

It is important that the silver oxide used should be freshly prepared and carefully dried. The oxide is most conveniently prepared by adding hot, filtered barium hydroxide solution to a hot solution of silver nitrate, washing the precipitated oxide with boiling water until all excess of barium hydroxide has

been removed, and drying the filtered substance first on a porous plate and afterwards in a steam-oven, the door of which remains open. The oxide should be finely powdered to facilitate the drying, and kept in a desiccator until required for use. Freshly prepared silver oxide appears to act with greater readiness than that which has been kept for some time.

As mentioned above, those substances are most readily alkylated which are soluble in alkyl iodides. If, however, the compound to be alkylated is insoluble in the alkyl halide, it may be dissolved in a neutral solvent such as acetone or benzene. In such cases the alkylation is slower, and is frequently incomplete after one treatment. In this connection it is to be noted that alkylation has the general effect of increasing the solubility of a substance in organic solvents. Hence if the substance under treatment is insoluble in the alkyl iodide used, and is one into which it is possible to introduce more than one alkyl group, then the partially alkylated product may be, and frequently is, soluble in the halide. This being so, an extraneous solvent is not required in the subsequent alkylation which is necessary to complete the reaction. The sugars furnish extreme cases of this kind. Cane sugar is so insoluble in organic solvents that in order to methylate it (19), it was found necessary by Purdie and Irvine to convert the sugar into a syrup by adding its own weight of water, to dissolve this in methyl alcohol, and then to add silver oxide and methyl iodide in small quantities at a time in order to prevent precipitation of the sugar by the iodide. Water, alcohol, and sugar were doubtless attacked simultaneously by the alkylating materials. The product from the first alkylation was soluble in methyl alcohol, and after three alkylations, in methyl iodide. The fourth and final alkylation was therefore conducted in methyl iodide solution, and a completely methylated product was thereby obtained.

If it is necessary to employ an extraneous solvent, the best method of procedure is to dissolve the substance in the

minimum amount of the hot solvent and to add the silver oxide and alkyl iodide in small, aliquot quantities.

The preparation of dimethyl *d*-dimethoxysuccinate (8) from methyl tartrate may be taken as a typical case of alkylation in the absence of a solvent. Methyl tartrate (1 mol.) is dissolved in methyl iodide (6 mols.), and dry silver oxide (3 mols.) is added in small quantities at a time. The reaction mixture is contained in a flask under a reflux condenser. The reaction, which is spontaneous and at first violent, is moderated by dipping the flask into cold water. Finally, when spontaneous action has ceased, the reaction is completed by heating the flask on a steam-bath for two or three hours. The product is then extracted by boiling ether, and the oil remaining after the removal of the solvent by distillation crystallises on nucleation. The silver residues are practically entirely composed of silver iodide, and the yield of dimethyl *d*-dimethoxysuccinate is almost quantitative.

It has already been mentioned that the alkyl iodides are the most suitable halides for this reaction. Of the iodides, methyl and ethyl iodides are most conveniently used, as the reaction is usually more complete with these than with the higher iodides (Lander (4)). The explanation of this fact is given in the discussion of the mechanism of the reaction.

The possibility of oxidation occurring during alkylation by means of silver oxide and alkyl iodides must not be lost sight of. The liability to oxidation depends on the conditions under which the experiment is carried out, and by consideration of these conditions may be almost entirely avoided.

It is not intended, in this paper, to give an exhaustive account of all the applications which have been made of the silver oxide reaction, as such an undertaking would involve a detailed description of the chemical research work in St. Andrews during the past thirteen years. A glance at the index to the literature will serve to show how numerous and varied have been the applications of the reaction, and further, that

its value has been tested by many workers outside St. Andrews. It is only possible to give a somewhat incomplete summary of the applications of the reaction to the preparation of different classes of substances, and at the same time to refer to the more important problems which have been solved by its aid.

Preparation of Substituted Acetic Acids and their Derivatives

In the course of a research the chief object of which was the determination of the optical effect of substituting alkyl groups for alcoholic hydrogen in active mandelic acid, McKenzie (3) prepared several phenylalkyloxyacetic acids. By alkylating *i*-mandelic acid or its esters with the appropriate alkyl iodide and silver oxide, he obtained products which on hydrolysis yielded *i*-phenylisopropoxy-, *i*-phenylethoxy-, and *i*-phenylmethoxy-acetic acids. Under similar conditions *l*-mandelic acid gave *l*-phenylethoxyacetic acid, *l*-phenylmethoxyacetic acid and its methyl ester, and *l*-phenylisopropoxyacetic acid. When *l*-mandelic acid was alkylated by silver oxide and propyl iodide, an ester was obtained which on hydrolysis yielded an inactive phenylpropoxyacetic acid. Partial racemisation also occurred during one of the preparations of *l*-phenylethoxyacetic acid.

The racemic methoxy-, and propoxy-phenylacetic acids prepared as above, together with a number of alkyloxysuccinic acids, have been most usefully employed by McKenzie and Harden (18) in an investigation on the biological method for resolving inactive acids into their optically active components. The results showed that the resolution is due to the mould attacking one optical isomeride more readily than the other, rather than to an attack by the organism on one isomeride exclusively. No attempt was made, in this work, to isolate a pure, active isomeride ; the detection of an optically active

product was sufficient for the purpose. Considering the superior activity of the alkyloxy-acids as compared with the corresponding hydroxy-acids, it will be seen how suitable the former are for work of this kind.

McKenzie's racemic methoxyphenylacetic acid has been used by Marckwald and Paul (37) in demonstrating Marckwald's general method for effecting asymmetric synthesis. By heating a racemic acid with an optically active base to a sufficiently high temperature it is theoretically possible, by reason of the inversion which active acids frequently undergo at high temperatures, to obtain a salt-mixture containing the *d*- and *l*-acids in unequal quantities. Thus inactive methoxyphenylacetic acid was heated with strychnine for eighteen hours at 150°-160° C., and from the mixture an acid was isolated, having a specific rotation of 0·32°.

McKenzie has himself utilised *dl*-phenylethoxyacetic, *dl*-ethoxypropionic and other acids in the course of important work which resulted in similar asymmetric synthesis (McKenzie and Thompson (29)). If one of these racemic acids be partially esterified with *l*-menthol, the acid remaining unesterified is laevorotatory; the ester so formed, when hydrolysed with potassium hydroxide, yields an acid which contains an excess of the *l*-form. These phenomena are due to the fact that the rate of formation of the ester *l*-base-*d*-acid is greater than that of the *l*-base-*l*-acid ester; the residual acid hence contains an excess of the *l*-isomeride. The *l*-base-*d*-acid ester which constitutes the larger portion of the ester formed, since it is formed more readily than the *l*-base-*l*-acid compound, is also hydrolysed more rapidly than the latter. During the earlier part of the hydrolysis, therefore, the *d*-acid is liberated in greater quantity than the *l*-acid, and in contact with the unused potassium hydroxide undergoes partial or complete racemisation. The remaining ester is now largely the *l*-base-*l*-acid form, and being hydrolysed by the reduced quantity of potassium

hydroxide gives the excess of the *l*-acid found at the end of the process.

The preparation by Lander (10) of derivatives of benzoylacetic acid is referred to in the section dealing with the alkylation of tautomeric compounds.

Preparation of Substituted Propionic Acids and their Derivatives

A simple means of preparing the alkyloxypropionates consists in the alkylation of the lactic esters by the silver oxide method. From methyl *l*-lactate, Purdie and Irvine (2) obtained methyl *l*-methoxypropionate by the action of silver oxide and methyl iodide, and, substituting ethyl for methyl iodide, they converted ethyl *l*-lactate into ethyl *l*-ethoxypropionate. These esters, on hydrolysis, yielded the corresponding alkyloxy-acids, and a number of metallic salts of the latter were prepared and examined. Further, the silver salts of these two acids were caused to react with alkyl iodides, and in this way ethyl *l*-methoxypropionate and methyl *l*-ethoxypropionate were prepared. This series of four esters, two acids and a number of metallic salts, all in active forms, furnished optical data of a nature which was, at the time, much required. With these data the authors were in a position to discuss the effect on the rotation of lactic acid of substitution of alkyl groups for hydrogen in the carboxylic group and in the alcoholic hydroxyl group. The general conclusions arrived at are beyond the scope of this paper.

It was pointed out in the Introduction that the alkyloxy-esters show, as a rule, considerably greater optical activity than the parent hydroxy-esters. This fact has been usefully employed by Irvine (33) in his resolution of lactic acid. This method of resolution depends on the fact that morphine *l*-lactate is much less soluble than the morphine salt of the *d*-acid. Lactic acid and the lactates are only feebly active

in solution, and it is hence difficult to determine whether an active product is entirely free from the corresponding inactive form. The difficulty was overcome by converting the supposedly pure *l*-acid, obtained as indicated above, into its methyl ester and alkylating the latter with silver oxide and methyl iodide, whereby methyl *l*-methoxypropionate was formed. The latter compound is highly active, and the rotation of the substance so prepared agreeing with that previously determined (Purdie and Irvine (2)), a strong guarantee of the purity of the *l*-acid was furnished. By this procedure experimental error is largely eliminated and traces of inactive material readily detected.

A number of the esters of the $\alpha\beta$-dimethoxypropionic acid derived from *d*-glyceric acid have been prepared by Frankland and Gebhard (27) for the purpose of tracing the effect on rotation of replacement by two methyl groups of the two hydroxylic hydrogen atoms in the esters of *d*-glyceric acid. The methyl, ethyl, propyl, butyl, heptyl, and octyl dimethoxypropionates were obtained by adding silver oxide (3 mols.) to a solution of the corresponding glycerate (1 mol.) and methyl iodide (6 mols.) in ether. The remaining procedure was as usual. It is worthy of note that these authors refer to the silver oxide reaction as ' the elegant method of alkylation discovered and elaborated by Purdie and his pupils. This reaction is of the very greatest value in alkylating optically active acids. . . .'

Preparation of Monoalkyloxy-Derivatives of Succinic Acid

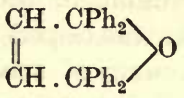
Mention has already been made of the preparation of ethyl *l*-ethoxysuccinate from ethyl malate by Purdie and Pitkeathly (1), who also obtained *l*-ethoxysuccinic acid by hydrolysis of the ester. A detailed study of monomethoxysuccinic acid and its methyl-, ethyl-, and propyl-esters has

been made by Purdie and Neave (57). The preparation of the methyl ester is readily accomplished by allowing methyl malate (1 mol.), silver oxide (2 mols.), and methyl iodide (4 mols.) to react spontaneously, completing the reaction by two hours' heating over a steam-bath, and finally extracting the product with boiling ether. After removal of the solvent the residual oil is dried and distilled under reduced pressure. Methyl *l*-methoxysuccinate is obtained in a chemically pure form after four such distillations, and its optical rotation is unchanged by further distillation. In a similar manner ethyl *l*-methoxysuccinate was prepared from ethyl malate, while the propyl ester was prepared by the interaction of silver *l*-methoxysuccinate and propyl iodide. From the methyl ester the active diamide and dianilide of *l*-methoxysuccinic acid were prepared by standard methods and their optical activity determined. The data so obtained form a useful addition to that which has already been gathered.

This work has been further extended by Purdie and the writer (58). By the action of phosphorus pentachloride, *l*-methoxysuccinic acid was converted into the corresponding acid chloride, no racemisation or inversion occurring during the reaction. By boiling the same acid with acetyl chloride, *l*-methoxy-succinic anhydride was prepared as an active liquid. One of the two possible isomeric methyl hydrogen *l*-methoxy succinates was obtained when this anhydride was dissolved in methyl alcohol, and the work further included the preparation of *l*-methoxysuccinamic acid.

The behaviour of methyl *l*-methoxysuccinate with the two Grignard reagents, magnesium methyl iodide and magnesium phenyl bromide, presents an interesting comparison. By interaction with the former, the active ditertiary glycol γ-methoxy-$\beta\epsilon$-dimethylhexane-$\beta\epsilon$-diol $HO.CMe_2.CHOMe.CH_2.CMe_2OH$, is produced and isolated in the form of its anhydride (Purdie and Arup (59)). During the reaction of the ester with magnesium phenyl bromide, however, the elements of

methyl alcohol are removed and two compounds are obtained which are both inactive and neither of which contain methoxyl. These are 2 : 2 : 5 : 5-tetraphenyl-2 : 5-dihydrofuran :—



and a triphenylbutyrolactone respectively. The same furan derivative is obtained by the action of magnesium phenyl bromide on methyl maleate.

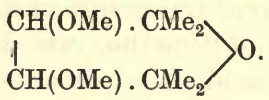
Preparation of Dialkyloxy-Derivatives of Succinic Acid

The first compound of this type to be synthesised by means of the silver oxide reaction was ethyl *d*-diethoxysuccinate, prepared by Purdie and Pitkeathly (1). The production of methyl *d*-dimethoxysuccinate from methyl tartrate by Purdie and Irvine (8) has already been described ; from ethyl tartrate, by treatment with silver oxide and methyl iodide, the same authors prepared ethyl *d*-dimethoxysuccinate. The crystalline *d*-dimethoxysuccinic acid is obtained from either of the methoxy-esters by hydrolysis with barium hydroxide, and subsequent decomposition of the barium salt by sulphuric acid. A number of normal and hydrogen-metallic salts of *d*-dimethoxysuccinic acid were prepared, and the determination of the rotation of these, and of the esters mentioned above, furnished material from which certain generalisations on the optical activity of this series of compounds could be drawn. *d*-Dimethoxysuccinamide was also prepared, but attempts to convert this into the corresponding imide, like other attempts made at a later date, were fruitless.

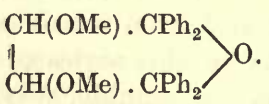
The work on the optical activity of methyl-, ethyl-, and propyl-dimethoxysuccinates was continued by Purdie and Barbour (9), who traced the influence of solvents on the

rotatory powers of these esters and of the corresponding tartaric esters.

Purdie and the writer (58) have prepared a series of dimethoxy-compounds similar to those derived from monomethoxysuccinic acid. It was hoped that information bearing on the tautomeric behaviour of succinyl chloride might be obtained by the study of its active analogue *d*-dimethoxysuccinyl chloride. Neither this compound nor *l*-methoxysuccinyl chloride, however, exhibited mutarotation when dissolved in indifferent solvents, and from these and other experiments it must be concluded that the substances do not consist of mixtures of dynamic isomerides. Treatment of methyl *d*-dimethoxysuccinate with magnesium methyl iodide yielded the laevorotatory $\gamma\delta$-dimethoxy-$\beta\epsilon$-dimethylhexane-$\beta\epsilon$-diol, $HO.CMe_2.CH(OMe).CH(OMe).CMe_2.OH$, which, as already mentioned, cannot be further methylated by the silver oxide reaction. When repeatedly distilled, the substance loses water and becomes converted into the dextrorotatory furan derivative:—



A corresponding compound is directly obtained when magnesium phenyl bromide is substituted for magnesium methyl iodide in the above reaction; this product is 3:4-dimethoxy-2:2:5:5-tetraphenyltetrahydro-furan:—



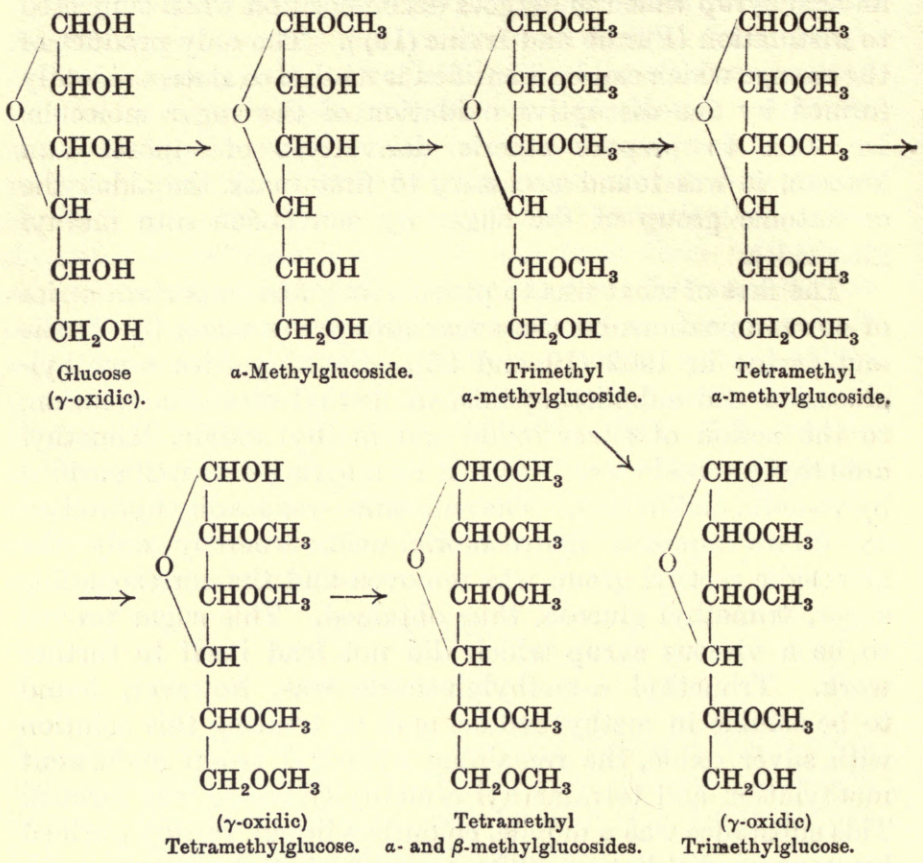
The Alkylation of Monosaccharides

Although benzoin and salicylaldehyde can be directly alkylated by the silver oxide method, the process is not directly

applicable to the simple hexoses. Glucose dissolved in methyl alcohol and treated with silver oxide and methyl iodide yields an acid syrup which undergoes decomposition when subjected to distillation (Purdie and Irvine (19)). The only product of the change which can be identified is methyl oxalate, evidently formed by the disruptive oxidation of the sugar molecule. In order to prepare etheric derivatives of aldoses and ketoses, it was found necessary to first mask the aldehydic or ketonic group of the sugar by conversion into methyl glucosides.

The first of what was to prove a long and important series of communications on the sugar group was made by Purdie and Irvine in 1902 (19 and 22). Starting with α-methyl-glucoside and submitting this, in methyl alcoholic solution, to the action of silver oxide and methyl iodide, trimethyl α-methylglucoside was obtained as a syrup, and was purified by vacuum distillation. The substance was readily hydrolised by dilute aqueous hydrochloric acid, whereby only the glucosidic methyl group was removed and the corresponding sugar, trimethyl glucose, thus obtained. This sugar proved to be a viscous syrup which did not lend itself to further work. Trimethyl α-methylglucoside was, however, found to be soluble in methyl iodide, and, on treating this solution with silver oxide, the remaining hydroxyl group underwent methylation and tetramethyl α-methylglucoside was formed. This substance was a mobile, colourless liquid, readily purified by vacuum distillation. The product of its hydrolysis with aqueous hydrochloric acid was found to be the crystalline sugar tetramethyl glucose, a body which afterwards played an important *rôle* in the chemistry of alkylated sugars. Finally, when tetramethyl glucose was itself subjected to alkylation, no oxidation occurred, but there resulted a mixture containing tetramethyl α-methylglucoside and a large excess of a crystalline isomeric substance. This crystalline substance was later proved to be, not a pentamethylated aldehydic

glucose, but tetramethyl β-methylglucoside (25). The changes described are represented as follows :—



It has not yet been ascertained which of the hydroxyl groups in α-methylglucoside remains unalkylated when it is converted into trimethyl α-methylglucoside, and hence the formula given for the latter substance may not be strictly accurate as regards the positions of the substituent methyl groups. Work at present being conducted by Professor Irvine tends to show, however, that the view adopted is correct.

On oxidation by Kiliani's method, tetramethyl glucose

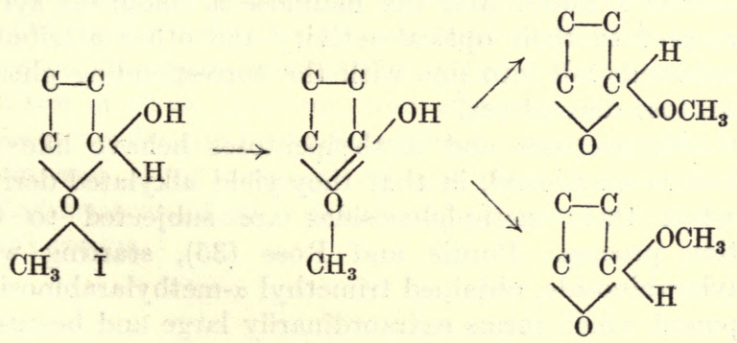
yielded tetramethyl gluconolactone. Bearing in mind the tendency of gluconic and similar acids to form γ-lactones, it will be seen that the unmethylated carbinol group in tetramethyl gluconic acid and in tetramethyl α-methylglucoside is that in the γ-position. It is therefore the γ-carbon atom in the methylated and in the parent glucosides which is united with the oxygen atom of the ring. These facts are of great importance, since they constitute what is probably the strongest experimental evidence in favour of Fischer's formula for glucosides.

It has been pointed out that, excluding a few doubtful exceptions, the silver oxide reaction does not cause racemisation of reacting substances; the sugars furnish a striking illustration of this point. Not only do the methylated compounds mentioned above retain optical activity, but they are chemically and optically more stable (if such a term may be used) than the corresponding unmethylated substances. It is beyond the scope of this paper to discuss, in a general manner, the results which have been obtained by the study of the optical activity of the methylated sugars and their compounds. These results are of importance, and are likely to prove of further value in any generalisations on the activity of the sugar group, since in the methylated compounds the constitutive influence of the hydroxyl groups is much modified, if not entirely eliminated.

Tetramethyl glucose, as was to be expected, is very soluble in organic solvents. It is therefore possible to examine the substance polarimetrically in solutions from which water is absent and in which no ionisation can occur. As is well known, the reducing sugars exhibit mutarotation in aqueous and in alcoholic solutions, and this mutarotation is now believed to be due to the interconversion, in such solutions, of the α- and β-forms of the dissolved sugar, these two forms being dynamic isomerides, differing in the position in space of the hydrogen and hydroxyl radicles attached to the terminal

carbon atom. The view prevails that the interchange of positions of the radicles cannot occur directly, but is due to rupture of the oxidic ring, and it has been suggested that the rupture is accompanied by union of the molecule with a molecule of water. The fact that tetramethyl glucose shows marked mutarotation in such solvents as benzene and carbon tetrachloride from which all traces of water have been carefully removed, at once disposes of all theories of the mechanism of the isodynamic change, which assume the addition of water or of alcohol to the molecule of the sugar (Purdie and Irvine (25)). Tetramethyl glucose can be obtained in two forms, the α- and β-isomerides, and these are similar, in their nature and mutarotation, to the corresponding varieties of glucose itself. Tetramethyl α-glucose, when dissolved in water, alcohol, benzene, toluene, or carbon tetrachloride, has initially a high dextro-rotation falling until a constant value is reached; the β-isomeride shows a low dextro-rotation initially, and this rises to the same equilibrium value. The values for the initial and equilibrium rotations are little affected by the nature of the solvent, a fact which seems to point to the elimination of the constitutive effect of the hydroxyl groups by methylation. This study of the alkylated glucoses and glucosides was continued by the correlation of the tetramethyl α-glucose with tetramethyl α-methylglucoside and of the β-sugar with the corresponding glucoside. Irvine and Cameron (28) completed the identification of tetramethyl β-methylglucoside by preparing it by direct alkylation of β-methylglucoside. The β-glucosides can therefore be alkylated by means of the silver oxide reaction in the same manner as their α-isomerides. The production of tetramethyl β-methylglucoside by alkylation of tetramethyl glucose in the usual manner has already been mentioned. Curiously enough, this alkylation proceeds at −10° C., and takes exactly the same course as when carried out at higher temperatures (Irvine and Moodie (36)). Further experiments by the same authors

supply an explanation of this apparent anomaly, and afford an insight into the mechanism of this particular case of alkylation. Such methylation might be supposed to proceed either by the intermediate formation of an additive compound of sugar and alkyl iodide and subsequent removal of hydrogen iodide, or by the intermediate formation of a silver derivative in which silver replaces the glucosidic hydrogen atom. In the latter alternative, if the β-sugar formed a silver derivative in this way and methyl iodide reacted with the resultant substance, the presence of a large excess of the β-glucoside in the product would be accounted for. This supposition is rendered unlikely, however, by the failure, after repeated attempts, to obtain any evidence of the formation of a silver derivative of tetramethyl glucose. On the other hand, solutions of tetramethyl glucose in alkyl halides showed remarkable abnormalities in optical activity at low temperatures, and these abnormalities (the details of which cannot be given here) can be explained by association between the sugar and the alkyl iodide. It appears probable, therefore, in view of the existing evidence of the occasional quadrivalency of the oxygen atom, that in this case alkylation occurs by intermediate formation of a methyl iodide additive compound from which hydrogen iodide is subsequently removed by the agency of silver oxide. The change may be represented schematically as follows :—



Mention should be made of the preparation of a number of alkylated glucose derivatives which have been prepared with the object of determining the constitution of the parent glucose compounds; these are referred to in a later section.

The methods which have been applied to the preparation of alkylated derivatives of glucose serve also for the production of similar compounds of other sugars. α-Methylgalactoside, when fully methylated, gives a colourless, liquid tetramethyl α-methylgalactoside, and on hydrolysis with dilute hydrochloric acid, the latter compound yields the corresponding sugar, tetramethyl galactose (Irvine and Cameron (26)). This substance differs from tetramethyl glucose in being an uncrystallisable syrup, and experiments on the mutarotation of the compound are therefore restricted, but not so far as to conceal the analogy between the two alkylated sugars. Further alkylation of tetramethyl galactose results in the production of a mixture of the stereoisomeric tetramethyl α- and β-methylgalactosides in which the β-isomeride is in large excess. The analogy is further exemplified by the fact that tetramethyl β-methylgalactoside is, like the corresponding glucoside, a crystalline compound. Again, by processes similar to those already described, Irvine and Moodie (31) from α-methylmannoside, have prepared tetramethyl α- and β-methylmannosides and tetramethyl mannose. In this case the methylated α-mannoside is a crystalline solid, the isomeric β-mannoside a liquid, and the mannose a colourless syrup. With respect to their optical activity and other attributes, the compounds fall into line with the corresponding glucose and galactose derivatives.

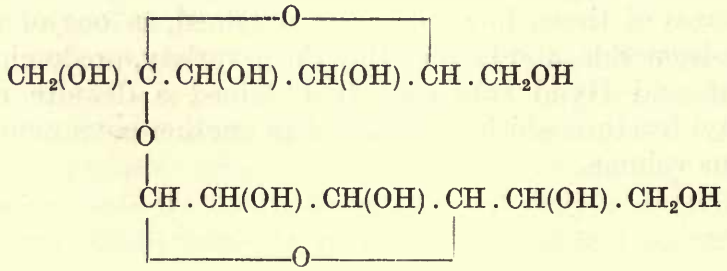
The aldo-pentoses and methylpentoses behave like the aldo-hexoses mentioned, in that they yield alkylated derivatives when their methylglucosides are subjected to the alkylation process. Purdie and Rose (35), starting with α-methylarabinoside, obtained trimethyl α-methylarabinoside, a compound which forms extraordinarily large and beautiful

crystals. Hydrolysis of the latter gave the syrupy sugar trimethyl *l*-arabinose, which, when alkylated in its turn, yielded a mixture of trimethyl α- and β-methylarabinosides containing a large excess of the latter isomeride. In the case of the methylpentose rhamnose, Purdie and the writer (34) obtained very similar results, with the exception that mixtures of the stereoisomeric α- and β-rhamnosides were dealt with throughout. The sugar trimethylrhamnose was identified by the formation of a crystalline hydrazone.

The only ketose to which the silver oxide reaction has so far been applied is fructose, and here much difficulty was encountered (Purdie and Paul (38); Irvine and Hynd (46)). As was the case with rhamnose, the glucosidic derivative used (methyl fructoside) could not be obtained in the crystalline form. The material initially subjected to alkylation was a syrupy mixture of the isomeric α- and β-methylfructosides possibly contaminated with other substances, and this, after treatment with silver oxide and methyl iodide and purification of the product by vacuum distillation and otherwise, yielded a liquid mixture of tetramethyl α- and β-methylfructosides. Considerable difficulty was experienced in isolating the products; this may have been due to the susceptibility of the ketoses and their derivatives to oxidation. The sugar obtained by hydrolysis of the alkylated fructoside mixture was syrupy, but by realkylating this and again hydrolising the product, a small quantity of crystalline tetramethyl fructose was eventually isolated. It was found impossible to prepare either of the pure tetramethyl α- or β-methylfructosides; mixtures of these, however, were obtained, in one of which the α-isomeride, and in the other the β-variety, predominated. Irvine and Hynd subsequently obtained a definite monomethyl fructose which is described in another communication to this volume.

The Alkylation of Disaccharides

The preparation of derivatives of disaccharides is a matter of difficulty on account of the readiness with which they undergo hydrolysis and of the insolubility of these substances in solvents other than water. The former difficulty does not apply to alkylation by means of the silver oxide reaction, and in the case of cane sugar, the solubility difficulty has been overcome by Purdie and Irvine (19, 22, and 30) by a method described in the Introduction. The materials were used in the following proportions: cane sugar (1 mol.), methyl iodide (20 mols.), silver oxide (10 mols.). Four alkylations with these proportions were necessary for the production, from ten grams of sucrose, of an equal weight of a neutral, syrupy liquid. This product received no purification beyond drying in a vacuum, but nevertheless gave analytical figures approximating to those required for an octamethylated sucrose. Hydrolysis of this substance by means of dilute, aqueous hydrochloric acid gave a syrup which reduced Fehling's solution and from which crystalline tetramethyl glucose has been obtained by simple nucleation. The uncrystallised portion of the last-mentioned syrup doubtless contained tetramethyl fructose, but the difficulties encountered in this work have so far prevented its isolation in a pure state. The results described are of considerable significance, since they afford direct experimental evidence of the correctness of Fischer's formula for cane sugar. According to this formula, cane sugar possesses a structure analogous to that of the alkylglucosides :—



Now it has been shown that methylglucoside and sucrose yield methylated derivatives when alkylated, and these two methylated substances yield the same tetramethyl glucose upon hydrolysis. It follows, therefore, that the constitution and linkage of the glucose group in sucrose must be the same as in the simple glucoside. In view of the experimental evidence, obtained in this work, bearing on the constitution of methylglucoside, it will be seen that the above formula is verified so far as it represents the glucose half of the molecule.

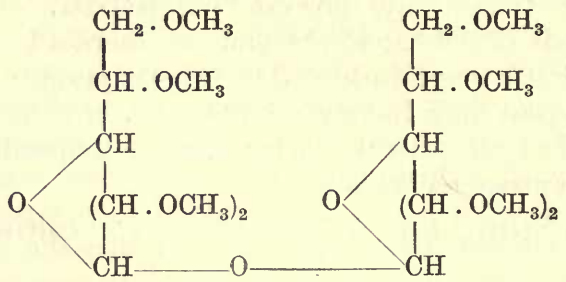
The only other disaccharide which has been alkylated by the silver oxide method is maltose. The sugar, in methyl alcoholic solution, was twice subjected to the action of silver oxide and methyl iodide, and the product being now soluble in methyl iodide, received two further treatments without the addition of alcohol. Methylation was here accompanied by oxidation of the free aldehydic group and subsequent esterification of the resultant carboxyl group. The viscid product was hydrolysed by dilute hydrochloric acid, and eventually yielded a syrup from which, after distillation in a vacuum, crystalline tetramethyl glucose was isolated. Evidence as to the mode of linkage of the glucose residues in maltose has been lacking, but was furnished by these experiments. Fischer suggested that such linkage might be either of an acetal or of a glucosidic type. In the latter case the molecule of maltose may be represented thus :—

$$\mathrm{CHO\,.\,(CHOH)_4\,.\,CH_2\,.\,O\,.\,\underbrace{CH\,.\,(CHOH)_2\,.\,CH}_{O}\,.\,CHOH\,.\,CH_2OH}$$

(or by the corresponding γ-oxidic formula). Whether the linkage be of the acetal or of the glucosidic nature, the glucose residue containing the free aldehydic group would undergo oxidation during alkylation. The remaining half of the maltose molecule would yield a pentamethyl glucose on hydrolysis of the alkylation product if the linkage were of the acetal form. But such is not the case; maltose cannot

therefore possess an acetal structure, and inspection of the above formula shows that it explains the production of tetramethyl glucose, under the conditions mentioned. The glucosidic linkage in maltose is thus confirmed.

The methylated sugars are more stable than the parent compounds, and so offer greater resistance to the destructive action of condensing agents than the latter. The alkylated sugars too are soluble in chemically indifferent solvents, and would thus appear to be available for the synthesis of methylated disaccharides. Tetramethyl glucose has, in fact, been used for such a purpose (Purdie and Irvine (30)). The sugar was dissolved in benzene containing 0·33 per cent. of hydrogen chloride, and the solution heated in a sealed tube at 105°-115° C. for ten hours. The product was a syrup which was subjected to two further treatments similar to the above. The resultant viscid liquid was purified by distillation in a vacuum, and was found to have no action on Fehling's solution. Condensation had evidently occurred, and the product proved to be an octamethyl glucosidoglucoside of the structure:



The formula represents three stereoisomerides, the $\alpha\alpha$-, $\beta\beta$-, and $\alpha\beta$-varieties, and the substance obtained was probably a mixture of all three modifications. This was the first recorded instance of the synthesis of a derivative of a non-reducing disaccharide, and a similar method of self-condensation has recently been adopted by Fischer for the preparation of disaccharides (*Ber.*, 1909, 42, 2776).

Determination of the Constitution of Sugar Derivatives by Means of the Alkylation Process

Reference has already been made to the evidence, obtained by means of the silver oxide reaction, bearing on the constitution of methylglucoside, sucrose, and maltose. These and other similar applications of the reaction have been collated by Irvine in a paper in the *Biochemische Zeitschrift* (50), which gives a useful summary and bibliography of such results of this nature as had been obtained prior to September 1909.

Of the natural glucosides, only salicin and gynocardin have so far been investigated by means of the reaction. The results obtained by Irvine and Rose (32) in the former case are of great interest, and show that salicin is constituted similarly to the artificial glucosides. By alkylation of the glucoside in the usual manner, a crystalline pentamethyl salicin was obtained. The hydrolysis of this compound by dilute aqueous acid led to the production of resinous substances which could not be further examined; it was therefore impossible to obtain evidence of constitution in this way. The following synthetic evidence, however, demonstrated the presence of the γ-oxidic linkage in salicin. Saligenin and tetramethyl glucose were dissolved in benzene containing 0·25 per cent. of hydrogen chloride, and the solution was heated in sealed tubes at 120° C. A syrupy, glucosidic condensation product resulted, which in all probability was a mixture of the α- and β-forms of tetramethyl salicin:—

$$CH_2(OH).C_6H_4.O.\underbrace{CH.(CH.OCH_3)_2.CH}_{O}.CH.(OCH_3).CH_2OCH_3.$$

The hydroxyl group remaining in this product was now alkylated, when a crystalline pentamethyl salicin resulted and

was found to be identical with the pentamethyl salicin obtained by direct alkylation of the glucoside. Thus salicin, like methylglucoside, possesses the γ-oxidic linkage as do also the related glucosides helicin and populin, which can be obtained from salicin by reactions which do not interfere with the glucosidic linkage.

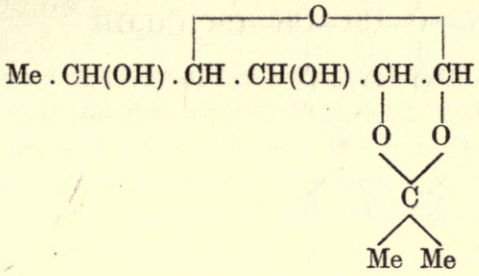
The alkylation process has also been applied by Moore and Tutin (55) to the natural glucoside gynocardin, or rather to the gynocardinic acid derived from it by the action of barium hydroxide and subsequent decomposition of the barium salt by sulphuric acid. The acid was methylated in the usual manner, first in methyl alcohol and afterwards in methyl iodide solution, and yielded methyl pentamethylgynocardinate; the two remaining hydroxyl groups resisted the action of the alkylating agents, and are therefore probably phenolic. The substance, like pentamethyl salicin, gave resinous products on hydrolysis by dilute acids, and no attempt was made to overcome this difficulty or to isolate the methylated sugar.

The hexoses readily form condensation compounds with acetone. The monoacetone derivatives are glucosidic, and, in their formation, one molecule of sugar unites with a molecule of acetone with the elimination of a molecule of water. Methylation of these compounds by means of the silver oxide reaction affords an insight into their structure. Acetonerhamnoside treated in this way yields a dimethylated derivative, and hence the formula suggested by Fischer for the parent compound,

$$\mathrm{Me\,.\,CH(OH)\,.\,\underbrace{CH\,.\,(CHOH)_2\,.\,CH}_{O}\,.\,O\,.\,CMe:CH_2},$$

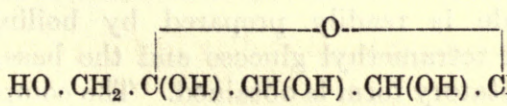
is excluded, since it contains three secondary hydroxyl groups. Dimethyl acetonerhamnoside is readily hydrolysed, yielding

the corresponding sugar dimethyl rhamnose, which forms a hydrazone but no osazone. Fischer's alternative formula for acetonerhamnoside

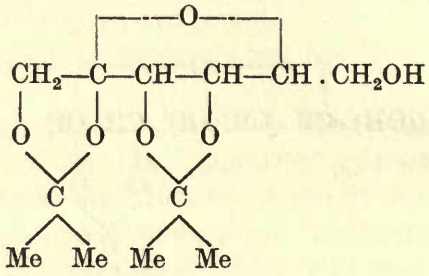


is therefore also excluded, since, in methylating the substance, of the two C-atoms attacked one is evidently in the α-position. It would appear that the second linkage of the acetone residue is attached to the β- or δ-carbon atom (Purdie and Young (34)).

By methylating fructose diacetone by means of silver oxide and methyl iodide, Irvine and Hynd (46) have obtained clear evidence of the structure of that compound, which evidently contains one hydroxyl group, since it yields only a monomethylated derivative. The latter substance is easily hydrolysed by dilute hydrochloric acid, giving a crystalline monomethyl fructose possessing all the properties of a reducing sugar. The sugar, when heated with phenylhydrazine, gives monomethylglucosazone, and when oxidised with bromine water, it is converted into a dihydroxymethoxybutyric acid which is incapable of forming a lactone. Consideration of these results will show that the formula for monomethyl fructose must be



and the following formula for fructose diacetone is thus probable :—



The various compounds obtained by condensation of fructose with acetone have been fully examined by Irvine and Garrett (54). In the course of this work a syrupy substance was obtained which was considered to be a mixture of the α- and β-forms of 2:3-fructosemonoacetone. The compound could not be sufficiently purified for analysis, but on methylating the substance by the same method as that employed for α-methylglucoside a liquid was obtained which could be purified by distillation in a vacuum. The product proved to be a trimethyl fructosemonacetone, and hence the substance from which it was prepared was shown to be a fructose monoacetone containing three hydroxyl groups.

Certain condensation compounds of glucose, such as the anilide and oxime, have hitherto been regarded as being derived from the aldehydic form of the sugar. Recent work, however (Irvine and Moodie (41)), in which the silver oxide reaction has been utilised, shows these compounds to possess the γ-oxidic linkage in the sugar residue, and they must therefore be considered to be derived from the α- and β-forms of the sugar and not from the aldehydic isomeride. Tetramethyl glucoseanilide is readily prepared by boiling an alcoholic solution of tetramethyl glucose and the base, and in this way a mutarotatory form is obtained. The compound

remains unaltered after several treatments with silver oxide and methyl iodide, and therefore has the formula—

$$CH_3O\,.\,CH_2\,.\,CH(OCH_3)\,.\,\underbrace{CH\,.\,CH(OCH_3)\,.\,CH(OCH_3)\,.\,CH}_{O}\,.\,NHC_6H_5.$$

Glucoseanilide is prepared in the same way as its tetramethyl analogue, and in its preparation and mutarotation Irvine and Gilmour (42) have obtained evidence of the existence of two stereoisomeric forms of the substance. Methylation of the compound (a matter of great difficulty by reason of its susceptibility to oxidation) led to the formation of a crystalline tetramethyl glucoseanilide, identical with that prepared as above. The constitution of glucoseanilide is thus established, and shown to be represented by the formula—

$$(HO)\,.\,CH_2\,.\,CH(OH)\,.\,\underbrace{CH\,.\,CH(OH)\,.\,CH(OH)\,.\,CH}_{O}\,.\,NH\,.\,C_6H_5.$$

(*a*- and *β*-forms)

It may be mentioned that the optical values for the two anilides obey Hudson's Law. Irvine and McNicoll (56) have extended this work to the anilides of tetramethyl mannose, tetramethyl galactose, and trimethyl rhamnose, and further, to the anilides of the parent unmethylated sugars, mannose, galactose, and rhamnose. Their results are in every way comparable with those described above.

Similar methods and reasoning have been adopted by Irvine and Moodie (41) and Irvine and Gilmour (42) in their work on glucoseoxime, which appears to be capable of reacting according to the structure—

$$HO\,.\,CH_2\,.\,CH(OH)\,.\,\underbrace{CH\,.\,CH(OH)\,.\,CH(OH)\,.\,CH}_{O}\,.\,NH\,.\,OH.$$

(*a*- and *β*-forms)

This compound is converted, by treatment with silver oxide and methyl iodide, into tetramethyl glucoseoxime methyl ether. The oximido-group is evidently methylated, along with the other hydroxyl groups, by the silver oxide reaction, and that this is generally the case is shown by the application of the reaction to other oximes. Thus œnanthaldoxime yields a monomethyl ether, while salicylaldoxime and benzoin oxime give dimethyl ethers under these conditions (Irvine and Moodie, *loc. cit.*).

Attempts have been made, by means of the silver oxide reaction, to obtain evidence bearing on the constitution of tetramethyl glucosephenylhydrazone, glucose phenylhydrazone, -*p*-toluidide, -*p*-phenetide, -*β*-napthylamide, and -*o*-carboxyanilide (Irvine and pupils (41, 42, and 56)). The compounds mentioned proved, however, to be so unstable that molecular rupture resulted, and the method had necessarily to be abandoned. The *o*-carboxyanilides of galactose, rhamnose, mannose, and maltose were found to be similarly unstable and to undergo decomposition when treated with silver oxide and methyl iodide (Irvine and Hynd (63)).

Preparation of Benzoin Derivatives

By interaction of benzoin, silver oxide, and ethyl iodide, Lander (4) obtained benzoin ethyl ether,

$$C_6H_5 . CH(OC_2H_5) . CO . C_6H_5.$$

The reaction was carried out at the boiling-point of the halide, and was seen to be accompanied by the formation of water and of very dark silver residues. This last fact was indicative of oxidation, and in addition to the benzoin ether, benzaldehyde and ethyl benzoate were formed during the reaction, probably as follows:—

$$\begin{cases} C_6H_5 . CH(OH) . CO . C_6H_5 + Ag_2O = C_6H_5 . CHO + C_6H_5CO_2H + 2Ag. \\ 2C_6H_5CO_2H + Ag_2O = 2C_6H_5CO_2Ag + H_2O. \\ C_6H_5CO_2Ag + C_2H_5I = 2C_6H_5CO_2C_2H_5 + AgI. \end{cases}$$

By substituting isopropyl iodide for ethyl iodide in the above reaction, and using benzene as a solvent, a mixture of unchanged benzoin, benzaldehyde, isopropyl benzoate, and the isopropyl ether of benzoin resulted.

Under improved conditions, however, it is possible by this process to convert benzoin practically quantitatively into an ether. Thus Irvine and Weir (40) effected the complete solution of the benzoin by adding acetone to the methyl iodide used, and by then proceeding with the alkylation in the usual manner obtained benzoin methyl ether in a purer state than the material prepared by Fischer's hydrochloric acid method.

Similarly Irvine and McNicoll (43) have succeeded in eliminating those secondary reactions which Lander found to accompany the formation of benzoin ethyl ether. The materials here used were benzoin (1 mol.), silver oxide (3 mols.), and ethyl iodide (9 mols.), dry ether being added until the boiling-point of the solution was reduced to 50° C. During the heating at this temperature the benzoin slowly passed into solution, and, after further heating at a slightly higher temperature, was converted into the benzoin ether. The yield was somewhat greater than 70 per cent. of the benzoin used.

The methylation of *o*-dimethoxybenzoin has been shown by Irvine (5 and 11) to proceed with perfect smoothness. The benzoin (1 mol.) is dissolved in excess of methyl iodide, and silver oxide (3 mols.) is gradually added. Gentle reaction takes place and is completed by 30 minutes' heating on the steam-bath. The product is extracted with ether and recrystallised from carbon bisulphide. In this way pure *o*-dimethoxybenzoin methyl ether is obtained in almost quantitative yield. The corresponding hydrobenzoin is insoluble in methyl iodide, and, in the absence of a solvent, resists alkylation by the silver oxide method. If hydrobenzoin itself, however, be brought into solution by the addition of acetone to the methyl iodide, vigorous action occurs

on the addition of silver oxide, and by repeating the alkylation, the crystalline hydrobenzoin dimethyl ether is obtained in good yield (Irvine and Weir (40)).

No alkylation occurs in the case of deoxybenzoin treated with silver oxide and ethyl iodide, since from such a reaction mixture Lander (10) was only able to separate unchanged deoxybenzoin and a little bidesyl. This result is confirmed by Irvine and Weir (40), who dissolved deoxybenzoin in methyl iodide and boiled the solution with silver oxide for twenty hours. The greater part of the substance was thereafter recovered unchanged; the remainder had been converted into bidesyl. Both these attempts to obtain derivatives of deoxybenzoin of an enolic character were therefore unsuccessful.

Irvine and Moodie (39) have made a detailed study of the reduction products of *o*- and *p*-dimethoxybenzoin. In the course of this work it was necessary to prepare anisoin methyl ether, and the preparation of this substance was found to proceed just as readily as that of the corresponding *ortho*-compound (*vide supra*). Prior to alkylation the anisoin was brought into solution by the addition of a small quantity of dry acetone to the methyl iodide required in the reaction.

As already indicated, two methods are available for the preparation of methyl- and ethyl-derivatives of such substances as benzoin, anisoin, *o*-dimethoxybenzoin, and furoin; these are the silver oxide method and Fischer's process, which consists in passing dry hydrogen chloride into methyl- or ethyl-alcoholic solutions of the substances in question. A comparative study of the two reactions has been made by Irvine and McNicoll (43), who find that the former reaction gives practically quantitative yields of the methyl ethers of the substances mentioned above, and that the ethyl ethers are likewise obtained in good yield and in such a condition that they readily crystallise. The hydrochloric acid method does not give very uniform results. In methyl alcoholic solu-

tion, furan derivatives are produced, and oxidation products further contaminate the alkyl ethers formed and render purification difficult. For further details illustrating the advantage of the employment of the silver oxide reaction in this direction, the original paper should be consulted. A modification of the usual procedure of alkylation was used by these authors in the methylation of furoin by the silver oxide method, and should be noted. The sparing solubility of this compound in methyl iodide and its ready oxidation to furil rendered the usual methods unavailable. Furoin methyl ether was, however, obtained by adding silver oxide to a solution of furoin in ethyl acetate to which had been added the requisite quantity of methyl iodide and also sufficient dry ether to reduce the boiling-point of the solution to 50° C.

Optically active benzoin has now been obtained by McKenzie and Wren (*Trans.*, 1908, **93**, 310), who prepared *l*-benzoin by the action of magnesium phenyl bromide on *l*-mandelamide. Wren (48) has since prepared a number of derivatives of *l*-benzoin, among them being the methyl ether. The method of alkylation by silver oxide and methyl iodide was utilised for this preparation in preference to the other method as being less likely to yield a racemised product; further, Fischer's method has been shown to yield a quantity of by-products (*vide supra*). *l*-Benzoin methyl ether was readily prepared by the method indicated, and is remarkable for the extraordinary influence of solvents on the rotation of the substance; the specific rotation varies from –88·2° (chloroform) to 147·8° (heptane).

In attempting to prepare *l*-benzoin ethyl ether by Fischer's method, Wren (49) found that complete racemisation occurred. *l*-Benzoin and alcoholic hydrogen chloride therefore interact to form *r*-benzoin ethyl ether. On ethylating *l*-benzoin by the silver oxide process, a partially racemised product was obtained, and it is very probable that the racemisation did not occur during the alkylation process but during the vacuum

distillation at a high temperature which was necessary to purify the substance.

In the course of an investigation of the racemisation phenomena observed in *l*-benzoin and its derivatives, McKenzie and Wren had occasion to prepare (53) the monomethyl ethers of both *i*- and *l*-triphenylethylene glycols. The alkylation of each of the parent glycols proceeded slowly, three treatments being necessary for completion. In each case alkylation of the secondary hydroxyl group alone occurred; the proof that this group was alkylated, and not the tertiary hydroxyl group, has already been referred to.

Preparation of Imino-Ethers

By the action of silver oxide and alkyl iodides on amides and substituted amides it is possible to prepare imino-ethers: a number of such preparations have been carried out by Lander, the sole worker in this field. Preliminary experiments (4) showed that benzamide was converted, by treatment with excess of silver oxide and ethyl iodide, into benziminoethyl ether, which was identified by conversion into the crystalline hydrochloride $C_6H_5 . C(OC_2H_5) : NH . HCl$. Under similar conditions, acetanilide yielded N-phenylacetiminoethyl ether $C_6H_5 . N : C(OC_2H_5) . CH_3$ or ethyl isoacetanilide, no trace of the isomeric N-ethyl ether being detected in the reaction product. When, however, methyl iodide was substituted for ethyl iodide in the reaction, the isomeric N-phenylacetiminomethyl ether $C_6H_5 . N : C(OCH_3) . CH_3$ and N-methylacetanilide $C_6H_5 . N(CH_3) . COCH_3$ were obtained in almost equal quantities (6). Analogous results were obtained by alkylation of aceto-*o*-toluidide, which is converted by silver oxide and ethyl iodide into N-*o*-tolylacetiminoethyl ether $CH_3 . C_6H_4 . N : C(OC_2H_5) . CH_3$ exclusively, while with silver oxide and methyl iodide it yields a mixture of the corresponding iminomethyl ether and N-methylaceto-*o*-toluidide $CH_3 . C_6H_4 . N(CH_3) . CO . CH_3$.

Aceto-*p*-toluidide differs from its *o*-isomer in being converted by silver oxide and methyl iodide into N-methylaceto-*p*-toluidide only. By similar methods, N-*α*- and N-*β*-napthylacetiminoethyl ethers were prepared from aceto-*α*- and aceto-*β*-napthalides, and N-phenylbenziminoethyl ether $C_6H_5 . N : C(OC_2H_5) . C_6H_5$ from benzanilide. The latter substance gives rise to the corresponding methyl ether mixed with a little benzoylmethylaniline when subjected to the action of silver oxide and methyl iodide (13) and the benz-*o*- and benz-*p*-toluidides behave similarly.

Under parallel conditions derivatives of oxalic acid yielded results in agreement with those already mentioned. Thus oxanilide was converted into di-N-phenylimino-oxalic diethyl ether $(C_6H_5 . N : COEt)_2$ and ethyl oxanilate into semi-N-phenylimino-oxalic diethyl ether. On the other hand, methyl oxanilate in benzene solution, when alkylated by means of silver oxide and methyl iodide, gave semi-N-phenylimino-oxalic dimethyl ether $CO_2Me . C : (NPh) . OMe$ along with some isomeric methyl phenylmethyloxamate $CO_2Me . CO . NMePh$ (24). The effect of ethylating methyl oxanilate in the usual manner was somewhat curious. A product intermediate in composition between $CO_2Me . C:(NPh)OEt$ and $CO_2Et . C:(NPh)OEt$ resulted, and interchange of alkyls in the carboxylic ester group must therefore have occurred during the ethylation of the $CO . NH$ residue.

A preliminary attempt to prepare a toluimino-ether from *o*-toluamide resulted only in the conversion of the latter into *o*-toluonitrile. This attempted alkylation was carried out in boiling alcoholic solution, and it was afterwards found that different amides (21), under the same conditions, give rise to nitriles together with some imino-ether. Thus whilst *o*-toluamide gives a 13·6 per cent. yield of the imino-ether, *p*-toluamide gives a 70 per cent. yield. This result is explained by supposing that the *o*-compound loses alcohol more readily than its *p*-isomeride: $C_7H_7 . C : NH . OEt \longrightarrow C_7H_7 . CN + EtOH$.

The silver oxide reaction has also proved to be of use in the preparation of certain of the aliphatic imino-ethers, which, as a class, are difficult to isolate and identify, by reason of their fugitive nature. If ethyl oxamate is treated with ethyl iodide and silver oxide a vigorous reaction ensues, and Nef's semi-imino-oxalic diethyl ether C : NH(OEt) . CO_2Et is produced (7). Acetamide undergoes decomposition under the same conditions. Alkylation of urethane takes place at the ordinary temperature if the substance is dissolved in a mixture of ethyl iodide and dry ether and the solution allowed to stand in contact with silver oxide for ten days. The product, imino-carbonic diethyl ether $(C_2H_5O)_2$: C : NH, is isolated in the form of the bromimino-ether.

It is seen that ethylation of substituted amides by silver oxide and ethyl iodide under the usual conditions gives imino-ethers . C(OEt) : N almost exclusively, while on substituting methyl for ethyl iodide imino-ethers and isomeric substituted amides are produced at the same time. It is however possible, as Lander (17) has shown, by conducting the alkylation at 100° C., to obtain both ethyl homologues PhN : C(OEt) . Me and PhNEt . CO . Me simultaneously, by the action of silver oxide and ethyl iodide on acetanilide. The results thus resemble those obtained by the methylation of the substance in an open vessel at 40°-50° C.

For comparative purposes, Lander investigated the action of silver oxide and methyl iodide on formanilide, and obtained N-phenylformiminomethyl ether H . C(OMe) : N . C_6H_5 mixed with a small quantity of the isomeric amide H . CO . NMe . C_6H_5 and some diphenylformamidine. When silver formanilide was boiled with ether and methyl iodide, a small quantity of imino-ether was formed, more of the amide and considerably more of the amidine than in the former experiment. These results are of considerable theoretical significance.

Alkylation of other Tautomeric Compounds

In his general investigation of the applicability of the silver oxide reaction (4) Lander tested the action of silver oxide and ethyl iodide on ethyl acetoacetate for the purpose of preparing, if possible, the isomeric ether in place of the alkyl compound formed by the action of sodium ethoxide and ethyl iodide. That is to say, it was hoped that ethyl acetoacetate would react in the enolic form as ethyl β-hydroxycrotonate and so be converted into ethyl β-ethoxycrotonate $CH_3 . C(OC_2H_5) : CH . COOC_2H_5$. The product of the reaction was fractionally distilled, and thus separated into the two substances ethyl ethylacetoacetate and ethyl β-ethoxycrotonate. As might perhaps have been expected, the yield of the latter was very small (5 per cent.). The simultaneous production of $. OC_2H_5$ and $: C . C_2H_5$ derivatives of ethyl acetoacetate may be regarded as evidence of the existence of both ketonic and enolic forms in the original substance. The fact that the product is largely composed of the ketonic derivative agrees with the physical evidence that ethyl acetoacetate exists, under ordinary conditions, mainly in the ketonic form.

When benzoylacetic ester is treated with the same reagents, the course of the reaction is entirely similar to that shown by acetoacetic ester, the alkylated product consisting very largely of the C-ethyl homologue $C_6H_5 . CO . CHEt . COOEt$ mixed with very small quantities of the isomeric β-ethoxycinnamic ester, $C_6H_5 . C(OEt) : CH . COOEt$ (Lander (10)). It would appear from these results that the silver oxide reaction, unlike the usual method of alkylating tautomeric substances of this type by which C-ethers only are obtained, does not interfere with the equilibrium between the dynamic isomerides of which the parent substance is composed.

Alkylation of ethyl ethylacetoacetate only occurred to a very slight extent (4) in an experiment carried out under

similar conditions to the above, and apparently the homologue of ethyl β-ethoxycrotonate was not one of the products. A modification of the usual alkylation process was tried by adding silver oxide to a mixture of ethyl acetoacetate and ethyliodoacetate. It was found necessary to cool the flask containing the reaction mixture and latterly to add benzene for the purpose of lowering the temperature. The product was purified by distillation in a vacuum and ethyl acetosuccinate was thus obtained. Silver oxide can therefore be substituted for sodium ethoxide in the synthesis of acyl-substituted succinic esters.

In contact with silver oxide and ethyl iodide, ethyl malonate does not react in the hydroxy-form to give β-diethoxyacrylate, but yields ethyl ethylmalonate as the sole product (*loc. cit.*).

Ethyl oxaloacetate and its silver derivative show similar behaviour in being completely converted by silver oxide and ethyl iodide into ethyl ethoxyfumarate EtOOC.C(OEt):CH.COOEt, which is also exclusively formed by interaction of the silver derivative and ethyl iodide. No C-ester is formed in either of the above reactions (Lander (17)).

The unsuccessful attempts to obtain alkylation derivatives of deoxybenzoin have already been referred to in the section dealing with benzoin derivatives.

The Mechanism of the Reaction

Prior to the discovery of the silver oxide reaction, dry silver oxide had been used as a synthetical reagent by Wurtz in the formation of ethyl ether from ethyl iodide (*Ann. Chem. Phys.*, 1856, iii. **46**, 222), by Erlenmeyer for a similar purpose (*Annalen*, 1863, **126**, 306), and by Linneman (*Annalen*, 1872, **161**, 37). In preparing isopropyl ether, Erlenmeyer used moist silver oxide. It is stated by Wurtz that dry silver

oxide and methyl or ethyl iodides react energetically immediately on coming into contact with one another, with evolution of much heat. Such, however, is not the case; Lander (4) found that with either iodide the reaction is slow, and he considers that interaction with the formation of ethers depends upon the presence, or initial formation, of small quantities of alcohol or water :—

$$Ag_2O+2C_2H_5OH = 2C_2H_5OAg+H_2O$$
$$C_2H_5OAg+C_2H_5I = (C_2H_5)_2O+AgI.$$

Purdie and Bridgett (20) record similar observations. Dry silver oxide shows no apparent change when heated with excess of methyl iodide, but when dry methyl alcohol is present the reaction starts immediately on warming and then proceeds spontaneously. In the course of two hours' heating on the water-bath, 35·5 per cent. of the silver oxide was converted into silver iodide in the former case, while in the latter 88 per cent. underwent the same change. The authors are of the opinion that in the absence of every trace of moisture and alcoholic substance, silver oxide and methyl iodide would not interact, and they share Lander's view that the Wurtz synthesis of ethers can only occur in the presence of traces of moisture which act catalytically in producing alcohols, these being afterwards alkylated. The statements which have been given are necessary in order to explain the apparent anomaly that silver oxide and an alkyl iodide should etherify a hydroxyl group in a compound rather than interact with one another with the formation of simple ethers. The anomaly is non-existent, since the statement of Wurtz is inaccurate. It must be remembered, however, that water is formed during alkylation by means of silver oxide and alkyl iodides, and that loss of the alkylating materials will therefore occur owing to simple ether formation in the manner mentioned above. If an alcoholic solvent is employed, the loss of the alkylating reagents is considerable. The necessity for the employment of a large

excess of the alkylating mixture in every case is therefore evident.

Certain of the higher alkyl iodides react more readily with silver oxide to form alkyl ethers than do methyl and ethyl iodides. It is possibly for this reason that the latter give better results in the alkylation process than, for instance, isopropyl iodide (Lander (4)).

There is little direct experimental evidence bearing on the mechanism of the silver oxide reaction, so that any conception of the course of the reaction must, for the present, be largely speculative. It is highly improbable that, in the alkylation of hydroxy-compounds, the silver oxide acts simply by removing hydrogen iodide, since no reaction occurs if litharge, zinc oxide, cupric oxide, or magnesium oxide are substituted for silver oxide. McKenzie (3) suggests that the most plausible hypothesis is that, by replacement of alcoholic H by Ag, an unstable silver derivative is formed and subsequently undergoes double decomposition with the alkyl halide.

The suggestion is endorsed by Lander (4 and 17) and by Purdie and Irvine (8). In accordance with this view, cuprous oxide might be expected to behave similarly to silver oxide. Alkylation of methyl tartrate by means of cuprous oxide and methyl or ethyl iodides has not been effected, but in the case of isopropyl iodide there is reason to believe that alkylation does take place, but imperfectly. (Private communication from Professors Purdie and Irvine.) The remarkable series of colour changes which are sometimes noticed during alkylation by this method might possibly be advanced as a further argument in support of the silver derivative hypothesis. It must, however, be admitted that, as yet, there is no positive evidence of the formation of a definite derivative of this kind during alkylation. Apparently the only attempt that has been made to isolate such an intermediate compound is that of Irvine and Moodie (36), already mentioned in connection with tetramethyl glucose. It is unlikely that alkylation of

hydroxy-compounds of the ordinary type proceeds by the formation of an oxonium additive compound with methyl iodide, as methyl tartrate, a substance which is most readily alkylated, shows no tendency to form such derivatives (Irvine and Moodie, *loc. cit.*). The methylation of tetramethyl glucose is undoubtedly brought about in this way by preliminary addition of methyl iodide and subsequent removal of the elements of hydrogen iodide from the oxonium compound by silver oxide, but this is to be regarded as an altogether exceptional instance.

Lander (4 and 17) takes the view that the first step in the alkylation of tautomeric compounds of the keto-enol character is the formation of silver derivatives of both isomerides, that is to say, OAg and CAg compounds; these subsequently undergo double decomposition with alkyl iodides, yielding the corresponding O- and C-alkyl derivatives.

The alkylation of amides and substituted amides has been supposed (4 and 17) to take place in a similar manner, by the intermediate formation of silver derivatives, but the recently published work of Matsui (64) appears to negative this view. It is shown that in the alkylation of amides such as acetamide and benzamide, silver oxide can be replaced by cuprous oxide, lead oxide, or even anhydrous potassium carbonate. These substances, and silver oxide also would therefore seem to act simply by removing hydrogen iodide.

It will thus be seen that the discovery of the silver oxide reaction has opened many lines of research, and it has proved to be of more immediate profit to pursue these lines of work rather than to closely scrutinise the reaction itself. Further discussion of the mechanism of the reaction must therefore be postponed until the present evidence has been considerably amplified.

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THE PREPARATION OF ANHYDRIDES OF ORGANIC ACIDS

THE reagents most frequently used for the preparation of anhydrides and chlorides of organic acids are the chlorine derivatives of phosphorous and phosphoric acids, and this notwithstanding the fact that these compounds are difficult to handle, and give rise in some cases to products contaminated with phosphorus compounds which are not easily removed. It thus appears remarkable that chlorides of other inorganic acids have not come into general use for similar purposes.

The inorganic chlorides generally, however, are no less troublesome to work with than those of phosphorus, but, apart from this, the number of such compounds available for practical purposes is limited. In the third group of the periodic system we have boron trichloride, but the cost of this compound at once puts it out of court as a reagent. In the fourth group occurs carbonyl chloride, the use of which as a means of preparing organic anhydrides has been suggested by Hentschel (*Ber.*, 1884, 17, 1285). Carbon tetrachloride does not appear to have been used, but the application of silicon tetrachloride to this purpose has been patented (U.S. Pat. 944372), as has that of silicon tetrafluoride (D. R. P. 171146). In the fifth group none of the chlorides except those of phosphorus have been employed: the action of nitrosyl chloride on silver salts is referred to below. In the sixth group we have sulphur with the numerous acids derived from its oxides. The most commonly occurring of the chloroanhydrides of these acids is sulphuryl chloride, and this compound has been used for anhydride formation, as has a mixture of sulphur dioxide and chlorine (*Abstr.*, 1906, i. 3, 621; D. R. P. 167304).

Chlorosulphonic acid and chlorosulphonates have also been employed (D. R. P. 146690; *Abstr.*, 1904, i. 282).

Sulphur tetrachloride, as is well known, does not exist under ordinary conditions, but thionyl chloride, which may be regarded as being related to sulphur tetrachloride in the same manner as phosphorus oxychloride is to phosphorus pentachloride, is a familiar reagent. This compound has been applied to the preparation of acid chlorides by H. Meyer, who prepared a number of acid chlorides by heating the free acid with five or six times its weight of thionyl chloride. He noticed that the anhydrides were formed in some cases (*Monatsheft.*, 1901, **22**, 777), and later (*Chem. Zeit.*, 1909, 1036) the same author outlines a method for the preparation of the anhydride of the sulphonic acids from thionyl chloride and the free acids of their potassium salts, apparently under similar conditions.

In the methods considered above, the formation of an anhydride is usually regarded as being due to the primary formation of an acid chloride, which then, on reaction with more anhydrous salt, gives rise to the anhydride and metallic salt. Thus, in the familiar example of phosphorus oxychloride, we have the following equations to represent the two stages in the reaction :—

$$2CH_3.COONa+POCl_3 = 2CH_3.CO.Cl+NaPO_3+NaCl$$
$$CH_3.COONa+CH_3.CO.Cl = (CH_3.CO)_2O+NaCl.$$

Similar reactions occur when other non-metallic chlorides, such as the chlorides of sulphur, are used.

The reaction which takes place between excess of the so-called sulphur dichloride and a dry salt of an organic acid was investigated by Heintz, who found that the chloroanhydride is formed among other products (*Jahresb. Chem.*, 1856, 569). Thus, using sodium benzoate, the reaction is represented by the equation :—

$$4C_6H_5.COONa+3SCl_2 = 2S+Na_2SO_4+2NaCl+4C_6H_5CO.Cl.$$

With excess of sodium benzoate the benzoyl chloride first formed yields benzoic anhydride.

Technical processes based on the above reactions have been patented by H. Kessler (D. R. P. 132605; *Abstr.*, 1903, i. 309) and by T. Goldschmidt (Eng. Pat. 25433; *J. Soc. Chem. Ind.*, 1910, 112, 592). Kessler specifies the use of sulphur dichloride SCl_2, while Goldschmidt causes excess of chlorine to react with the dry sodium salt in presence of sulphur. The acid chloride is thus formed, and the mixture on being heated gives the anhydride.

Carius (*Annalen*, 1858, **106**, 291) investigated the reaction between equimolecular proportions of sodium chloride and sulphur monochloride S_2Cl_2, both in the presence and in the absence of solvent, and found that although the reaction is not altogether smooth, the initial and final stages are represented essentially by the equation :—

$$2C_6H_5.COONa+2S_2Cl_2 = 2C_6H_5.CO.Cl+2NaCl+SO_2+3S$$

Gerhardt proposed another method for the preparation of organic anhydrides, in which the mechanism of the reaction is somewhat different from that described above for cases in which inorganic chlorides are used. This method is based on the observation that an organic acid chloride, such as benzoyl chloride, gives a mixed anhydride on reaction with a metallic salt of a different organic acid, according to the equation :—

$$CH_3.COONa+C_6H_5.CO.Cl = CH_3.CO.O.CO.C_6H_5+NaCl.$$

Such mixed anhydrides are unstable, so that on being heated they decompose with formation of the simple anhydrides :—

$$2CH_3.CO.O.CO.C_6H_5 = (CH_3.CO)_2O+(C_6H_5.CO)_2O.$$

Mixed anhydrides can also be prepared by heating excess of an anhydride such as acetic anhydride with another acid (Autehrieth, *Ber.*, 1887, **20**, 3188).

Consideration of the above reactions suggests at once the possibility of preparing organic anhydrides by formation and subsequent decomposition of mixed anhydrides of organic and inorganic acids; such mixed anhydrides are known, and, like those which contain organic radicals only, they are unstable and readily undergo a similar decomposition. Thus Pictet and his colleagues (*Abstr.*, 1903, i. 309, 456, 675; 1906, i. 3) have prepared mixed anhydrides of acetic acid with boric, arsenious, phosphoric, sulphuric, and nitric acids respectively by the interaction of glacial acetic acid or of acetic anhydride with the inorganic anhydride, while Francis (*Ber.*, 1906, 39, 3798) has prepared benzoyl nitrate from benzoyl chloride and silver nitrate, and Francesconi and Cialdea (*Abstr.*, 1903, i. 788; 1904, i. 707) have made mixed anhydrides of nitrous acid and organic acids by the interaction of nitrosyl chloride and silver salts of organic acids.

In the methods already described, in which sulphur dichloride is used, the reactions are carried out in absence of solvent, and the primary product is the acid chloride; while Carius, using equimolecular proportions of sulphur monochloride and sodium benzoate in equimolecular proportions, obtained benzoyl chloride even when he used carbon disulphide as solvent. By a modification of the conditions under which Carius worked, the writer has succeeded in preparing a series of acyl derivatives of the unknown acid, thiosulphurous $S_2(OH)_2$, of which sulphur monochloride may be regarded as the chloride. Thus, if dry sodium benzoate (2 mols.) and sulphur monochloride (1 mol.) are boiled together in presence of carefully dried ether or other indifferent solvent, the yellow colour of the sulphur chloride quickly disappears, and, after filtration from the sodium chloride formed in the reaction and concentration, the solution deposits crystals of benzoyl thiosulphite. The reaction is represented by the equation:—

$$2C_6H_5.COONa+S_2Cl_2 = (C_6H_5.CO)_2S_2+2NaCl.$$

Benzoyl thiosulphite crystallises in well-defined colourless crystals.

	Sulphur.	Molecular Weight (in Benzene F.P. Method).
Found, ...	21·32 per cent.	281
$(C_6H_5COO)_2S_2$ requires .	20·92 per cent.	306

The compound is extremely unstable and soon turns yellow owing to spontaneous decomposition, the products of which are benzoic anhydride, sulphur dioxide and free sulphur, as shown by the equation :—

$$2(C_6H_5COO)_2S_2 = 2(C_6H_5CO)_2O+SO_2+3S.$$

That the formation and decomposition of this substance take place quantitatively is shown by the following Table, where the weights are given of the crude products from 3·4 grams of sulphur chloride and 12·5 grams (instead of 11·5 grams) of silver benzoate. The theoretical quantities are calculated by means of the above equations from the weight of sulphur chloride used :—

	Calculated.	Found.
Weight of benzoyl thiosulphite (after filtration from silver chloride and distillation of ether), ...	7·6 g.	7·5 g.
Weight of sulphur (residue after extraction of the benzoic anhydride with ether),	0·95 g.	0·90 g.
Weight of anhydride (after distillation of ether from the ethereal extract), .	5·65 g.	5·60 g.

The method is widely general, and has been applied to a large number of unsubstituted fatty and aromatic acids and to acids containing halogen and nitro groups, the reactions in all cases being exactly similar to those just described: with acids of high molecular weight such as stearic and naphthoic acids the last traces of sulphur cannot be completely removed. In general, after the decomposition of the intermediate compound is complete, a change which is accelerated, as would be expected, by the application of heat, the anhydride can be

extracted by means of ether and can be freed from traces of sulphur by recrystallisation.

An even simpler way to prepare acid anhydrides is afforded by the employment of thionyl chloride in the same manner. If a solution of this reagent in ether is shaken with an organic silver salt, immediate reaction occurs, but usually no intermediate compound can be isolated, so that after filtration from the silver chloride the anhydride can be crystallised in a pure condition from the filtrate :—

$$2C_6H_5 . COOAg + SOCl_2 = (C_6H_5 . CO)_2O + SO_2 + 2AgCl.$$

The yield of anhydride by this method is nearly quantitative, even although only small quantities are prepared. Thus, in one experiment, 2·1 grams of crude but nearly pure benzoic anhydride were obtained instead of the calculated quantity, 2·3 grams. The method is applicable to the preparation of anhydrides of fatty and aromatic acids, both of small and large molecular weights, to the preparation of anhydrides of halogen and nitro acids and of some dibasic acids.

The use of a solvent is an essential feature of the new methods, and it is important that the solvent be carefully dried if successful results are to be obtained.

The low temperature at which these reactions occur, and the smooth manner in which they proceed, suggested their application to the preparation of normal anhydrides of hydroxy-acids, a type of compound which cannot be obtained by the methods hitherto in use, since by the employment of chlorides of phosphorus chlorination occurs, while, by the influence of heat, anhydro-acids and similar compounds are produced.

It was found, however, that with sulphur chloride and salts of glycollic, mandelic and malic acids the reaction is abnormally slow, while with salts of the hydroxybenzoic acids it is irregular, so that it is improbable that the normal anhydrides of the hydroxy-acids can be prepared by the use of this reagent.

Experiments with thionyl chloride gave more promising

results. Reaction takes place immediately, and proceeds apparently as smoothly as with acids of other types. Silver glycollate gave an intermediate compound which can be isolated in the pure state, while similar derivatives of mandelic and malic acids were obtained, but not pure.

If to silver glycollate suspended in ether, an ethereal solution of thionyl chloride be added, immediate reaction occurs, and, after filtration, there is obtained, on addition of light petroleum, a white crystalline substance, the composition of which is in agreement with the formula $[CH_2(OH)COO]_2SO$. It loses sulphur dioxide when allowed to stand, but only slowly. When nearly all the sulphur dioxide has been evolved there is left, after washing with ether, a white powder the composition of which agrees with that required by the formula $[CH_2(OH)CO]_2O$. It is inadvisable to hasten the decomposition by the application of heat, as a syrup is then formed which cannot be caused to crystallise, and elevation of temperature favours the formation of anhydro-compounds other than the normal anhydride. The anhydride melts at about 100°, is almost but not completely soluble in water, and appears to be different from the anhydride obtained by Fahlberg by the action of sulphur trioxide on glycollic acid (*J. Pract. Chem.*, [2], 7, 336). The manner of formation of this compound would point to its having the normal structure, were it not for the comparative stability of the intermediate compound. It is possible that in this reaction silver glycollate behaves in the abnormal manner sometimes displayed by silver salts of hydroxy-acids, and the participation of the hydroxyl group in the reaction is therefore not excluded.

With silver mandelate the tendency to form chlorinated products is pronounced, and the consequent formation of water has made it impossible to isolate the intermediate compound free from admixture with acid. The chlorine-containing impurities may be removed by repeated precipitation of the substance from its ethereal solution by means of

light petroleum; the relatively large quantity of even carefully dried solvent thus necessary tends, however, to the introduction of traces of water and consequent formation of more free acid. In absence of water the decomposition of the intermediate compound proceeds very slowly, and it is necessary to assist the decomposition by application of heat. After decomposition is complete a glass is obtained on extraction with benzene and subsequent removal of the solvent, the analytical figures for which agree nearly with those required for a compound $[C_6H_5.CHOH.CO]_2O$, while the figures obtained on titration point also to this formula. From this substance, which still contained a trace of sulphur, mandelic acid was regenerated by treatment with water or by dissolving in sodium hydroxide solution and acidifying, though a small portion remained undissolved by the solvents.

The intermediate compound formed from silver malate is more easily decomposed, and most of the sulphur dioxide can be expelled by passing carbon dioxide through the ethereal solution for a day or two. After distillation of the ether, soft feathery crystals separate from the residual syrup, and these, after washing with ether and recrystallisation, give analytical figures which agree nearly with those required for malic anhydride $\begin{matrix} CH(OH)CO \\ | \\ CH_2.CO \end{matrix}\!\!>\!O$. The substance is soluble in water, and malic acid is formed in the aqueous solution on standing. This substance is probably not the same as the porcelain-like anhydride of malic acid obtained by Walden (*Ber.*, 1899, 2706, 2819). It appears to be optically active. A fuller investigation of these interesting compounds must be deferred until they can be prepared more easily and in larger quantity. The experimental difficulties met with in their preparation are at present considerable.

Attempts to prepare normal anhydrides of the aminobenzoic acids were unsuccessful by both methods.

SUMMARY OF RESULTS

Type of Acid	Behaviour of Silver Salt towards Sulphur Chloride	Behaviour of Silver Salt towards Thionyl Chloride
Fatty Acids	Reaction normal. Intermediate compounds: Oils.	Reaction normal. No intermediate compounds.
Aromatic Acids	Reaction normal. Intermediate compounds: Crystalline Solids.	Reaction normal. No intermediate compounds.
Dibasic Acids	Anhydrides already known formed. No intermediate compounds isolated.	Anhydrides already known formed. No intermediate compounds.
Acids which contain halogen (fatty and aromatic)	Reaction normal. Intermediate compounds less stable than those from the unsubstituted acids.	Reaction normal. No intermediate compounds.
Nitro-aromatic Acids	Reaction normal. Intermediate compounds sparingly soluble in the usual solvents.	Reaction normal. No intermediate compounds.
Aromatic Amino-Acids	Reaction abnormal.	Reaction abnormal.
Hydroxy-Acids	Reaction varies. Intermediate compounds formed.	Reaction varies. Intermediate compounds formed.

The Constitution of Sulphur Monochloride

If we may look upon the glycollyl intermediate compound described above as a mixed anhydride of glycollic and sulphurous acids, that is, as a representative of the intermediate compounds whose existence in the case of non-hydroxy acids is too fugitive to be observed, the analogy between the course of the reactions when thionyl chloride is used, and those with sulphur chloride, is pronounced. The resemblance becomes complete when it is remarked that the decomposition of the acyl thiosulphites proceeds as a reaction of the first order. That such is the case has been ascertained by absorbing the sulphur dioxide evolved on its decomposition in iodine solution. The decomposition is conveniently carried out in toluene, maintained at its boiling-point, in a flask provided with a reflux condenser and gas delivery tube; the latter is branched, and each branch connected through a stopcock with absorption bulbs. In this way, if a regular current of carbon dioxide is passed through the flask, the quantity of iodine used from time to time, and thus the amount of decomposition, is readily determined by titration with sodium thiosulphate. One such set of observations is here given :—

Time in Minutes	x=cc. Iodine	$a-x$	$\frac{1}{t}\log\frac{a}{a-x}$
16	9·08	62·14	0·0059
26	21·38	49·84	0·0060
45	32·97	38·25	0·0060
71	43·71	27·51	0·0058
85·5	48·22	23·00	0·0057

Total quantity of iodine used after some hours=a=71·22 cc.

The fact that the decomposition of benzoyl thiosulphite is monomolecular may be taken as pointing to the transient

existence of thiosulphurous anhydride S_2O, and, if this is so, we should then have the following schemes to represent the course of the reactions with sulphur chloride and thionyl chloride respectively :—

Sulphur Chloride

$$2C_6H_5 . COOAg + S_2Cl_2 = (C_6H_5 . COO)_2S_2 + 2AgCl,$$
$$(C_6H_5 . COO)_2S_2 = (C_6H_5 . CO)_2O + S_2O,$$
$$2S_2O = SO_2 + 3S.$$

Thionyl Chloride

$$2C_6H_5 . COOAg + SOCl_2 = (C_6H_5COO)_2SO + 2AgCl,$$
$$(C_6H_5 . COO)_2SO = (C_6H_5 . CO)_2O + SO_2.$$

These methods of anhydride formation would thus be classified with that in which an unstable mixed anhydride is first formed by the action of benzoyl chloride on a salt of an organic acid.

The analogous behaviour of thionyl chloride and sulphur chloride may be further developed. If the reaction between thionyl chloride and silver benzoate be carried out, as already described in presence of ether, but with equimolecular proportions of the reagents, benzoyl chloride is obtained. With sulphur chloride the further reaction does not take place so readily, but it may be brought about by boiling benzoic anhydride with the chloride. Sulphur dioxide is then evolved and sulphur is liberated. The reactions may be represented by the equations :—

$$(C_6H_5 . CO)_2O + S_2Cl_2 = 2C_6H_5 . CO . Cl + S_2O,$$
$$2S_2O = SO_2 + 3S.$$
$$(C_6H_5 . CO)_2O + SOCl_2 = 2C_6H_5 . CO . Cl + SO_2.$$

This manner of viewing sulphur chloride as a chloro-anhydride the parent acid of which is extremely unstable, allows of some of its reactions being expressed very simply.

For example, its decomposition by means of water to give hydrochloric acid, sulphur dioxide, and free sulphur :—

$$S_2Cl_2+2HOH = S_2(OH)_2+2HCl$$
$$2S_2(OH)_2 = (2S_2O+2H_2O) = 3S+So_2+2H_2O.$$

The general resemblance between sulphur and oxygen compounds led Carius (*Annalen*, 1858, **106**, 291) to regard sulphur chloride as being sulpho-thionyl chloride, so that its formula should be—

$S:S\begin{matrix}Cl\\Cl\end{matrix}$ corresponding to $O:S\begin{matrix}Cl\\Cl\end{matrix}$ and not Cl . S . S . Cl.

He looked upon the reaction between sodium benzoate and sulphur chloride, in which benzoyl chloride is formed, as taking place in two stages, in the first of which benzoyl sulphide and thionyl chloride are produced :—

$$2C_6H_5 . COONa+2S_2Cl_2 = (C_6H_5CO)_2S+2SOCl_2+Na_2S$$
$$= 2C_6H_5 . CO . Cl+2NaCl+SO_2+3S,$$

while he formulated the reaction between sulphur chloride and water similarly :—

$$2H_2O+S_2Cl_2 = H_2S+2HCl+SO_2$$
$$2H_2S+SO_2 = 2H_2O+3S.$$

It is thus evident that Carius, having in mind the possible analogy between thionyl chloride and sulphur chloride, looked upon reactions in which the latter substance and oxygen-containing compounds take part as consisting in the primary formation of thionyl chloride, which then may react further.

As already shown, however, it is possible to view these reactions more simply, and to express, perhaps more clearly, the analogy between the two chlorides, although at the same time it should be noted that the analysis of the mechanism of these reactions previously detailed holds good for either constitutional formula. The similarity in the reaction of

the two compounds, though general, are similarities in behaviour common to acid chlorides, but if one takes into account the far-reaching analogy between oxygen and sulphur compounds, they may be held as pointing to similarity in constitution.

The amides corresponding to thionyl chloride and sulphur chloride are unknown, but Michaelis has prepared the tetra-alkylated derivatives of these compounds by the action of thionyl chloride (*Ber.*, 1895, **28**, 1016) and of sulphur chloride (*loc. cit.*, 165) respectively on dialkylamines in presence of ether, the reactions in each case being quite parallel :—

$$SOCl_2+4NH(C_2H_5)_2 = SO[N(C_2H_5)_2]_2+2NH(C_2H_5)_2 . HCl.$$
$$S_2Cl_2+4NH(C_2H_5)_2 = S_2[N(C_2H_5)_2]_2+2NH(C_2H_5)_2 . HCl.$$

The existence of amides and acyl derivatives of thio-sulphurous acid makes it appear probable that corresponding esters might also be obtained, and such compounds have been described by Lengfeld (*Ber.*, **28**, 449), who investigated the reactions which take place between sulphur chloride and the methoxide and ethoxide of sodium respectively in presence of light petroleum. The writer has not, however, succeeded in preparing these compounds either by Lengfeld's method or by modifications of it.

What appears to be direct evidence in favour of the sulphothionyl constitution of sulphur chloride is afforded by its formation from thionyl chloride by the action of phos-phorus pentasulphide :—

$$P_2S_5+5\,O:SCl_2 = P_2O_5+5\,S:SCl_2 \qquad \text{(Carius, } loc.\ cit.\text{)}$$

but according to Prinz (*Annalen*, **223**, 355) the change does not occur directly.

The converse transformation, that of sulphur chloride into thionyl chloride, can be effected by the action of sulphur trioxide at a temperature of 75°-80°.

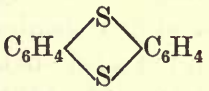
$$SO_3+S_2Cl_2 = SOCl_2+SO_2+S.$$

This reaction forms indeed the basis of a method for the preparation of thionyl chloride, for if a current of chlorine be passed into the mixture the liberated sulphur is reconverted into sulphur chloride, which then reacts with a further quantity of trioxide (D. R. P. 139455; *Abstr.*, 1902, ii. 420).

The behaviour of sulphur chloride towards hydrocarbons and phenols may be noticed. Boeseken (*Rec. Trav. Chim.*, 1905, **24**, 209) found that benzene and sulphur chloride react together in presence of aluminium chloride, so that diphenyl sulphide and free sulphur are formed quantitatively according to the equation :—

$$2C_6H_6+S_2Cl_2 = (C_6H_5)_2S+S+2HCl,$$

while Cohen and Skirrow (*Trans.*, 1899, **75**, 887) obtained diphenylene disulphide



and free sulphur from the same substances when aluminium chloride was employed as catalyst.

The reaction between phenol and sulphur chloride is vigorous, and among the products are dihydroxy-diphenyl sulphide $S(C_6H_4OH)_2$, free sulphur, and probably a disulphide $S_2(C_6H_4OH)_2$. Somewhat similar products were obtained by Henriquez (*Ber.*, 1894, **27**, 2992) from sulphur chloride and naphthol.

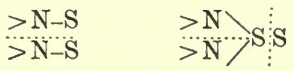
If we accept the unsymmetrical formula $S:SCl_2$ we can readily understand that the divalent sulphur atom may easily be split off in all the above cases with formation of a monosulphide :—

$$R_2S:S \rightarrow R_2S+S,$$

while with the symmetrical formula Cl. S. S. Cl the formation of a monosulphide is less intelligible.

The salt-like metallic derivatives of imides react with sulphur chloride though less readily than ordinary metallic

salts. Thus if silver succinimide (2 mols.) is shaken for some time with sulphur chloride (1 mol.) in presence of dry benzene, there is obtained, after filtration and evaporation of the benzene *in vacuo*, a quantitative yield of sulphur succinimide as a white crystalline powder which is stable when dry but decomposes fairly readily when in solution in such solvents as acetone. It is at once decomposed by sodium hydroxide solution. The molecular weight of this compound, as determined experimentally, points to the formula $[C_2H_4(CO)_2.N]_2S_2$. Silver phthalimide does not react smoothly with sulphur chloride, but, from potassium phthalimide, the sulphur derivative can be obtained though the yield is not very good. It is remarkable that the values found for the molecular weight of sulphur phthalimide agree with the simple formula $C_6H_4.(CO)_2NS$, a fact which, taken in conjunction with the quantitative yield of the bimolecular succinimide derivative, points to the unsymmetrical formula for sulphur chloride, as is indicated by the formulæ :—



a consideration of which shows that a theoretical yield of the monomolecular substance might be obtained by the breaking down of the double molecules of symmetrical structure, but less probably by the breaking down of those of unsymmetrical structure.

Sulphur phthalimide can be prepared in good yield by acting on phthalimide with excess of sulphur chloride and pyridine in presence of an indifferent solvent. It is a stable substance which crystallises from chloroform in colourless crystals which contain chloroform of crystallisation. Like the succinimide compound, it is at once decomposed by sodium hydroxide solution.

Thionyl chloride and silver succinimide when shaken together in presence of benzene appear to give the thionyl

compound corresponding to sulphur succinimide, but this substance has not been obtained in the pure state owing to its extreme sensitiveness to moisture, with which it at once gives sulphur dioxide and succinimide :—

$$[C_2H_4(CO)_2N]_2SO+H_2O = 2C_6H_4(CO)_2NH+SO_2.$$

It is seen from the foregoing that while neither formula for sulphur chloride is in conflict with the behaviour of this compound towards water, metallic salts and amines, the unsymmetrical one $S:SCl_2$ affords a better explanation of its reactions with hydrocarbons, phenols, and metallic derivatives of imines, and is therefore to be preferred, quite independently of any presumption in its favour from the standpoint of analogy.

WILLIAM SMITH DENHAM

INDIUM AND THALLIUM IN CRYSTALLOGRAPHICAL RELATIONSHIP

Introductory

Except in the case of the double sulphates (1), isomorphous relationships between salts of indium and thallium have not been made the subject of investigation. The literature dealing with the crystallography of indium salts is in fact remarkably scanty. Thiel and Koelsch (2) have described an oxide of indium—presumably In_2O_3—which crystallises in octahedra, with spinel habit, like Fe_3O_4. The compound In $F_3 3H_2O$ crystallises, according to Thiel (3), in four-sided, probably rhombic, prisms. No similar compound of other trivalent metal has been investigated crystallographically, and no compound of the type $MF_3 3H_2O$, where M=Al, Tl, Ga, has hitherto been isolated. Some interesting cases of isomorphism among the silicotungstates of the trivalent metals, including indium, have been studied by Wyrouboff (4). Thus in the series of salts $R_4(W_{12}SiO_{40})_3$ $60H_2O$, where R=Al, Fe, Cr, Ga, Bi, the results furnished by Wyrouboff are interpreted by Groth (5) to indicate isomorphism in the case of the salts of Al, Fe, Cr, Ga, and similarity of axial angle, though considerable divergence in axial constants, in the salt of Bi, and in $In_4(W_{12}SiO_{40})_3$ $63H_2O$, which differs from the other salts by three molecules of water of crystallisation. The series $R_4(W_{12}SiO_{40})_3$ $87H_2O$, where R=Al, Cr, Ga, is undoubtedly isomorphous. The members of the two series $R_4(Mo_{12}SiO_{40})_3$ $93H_2O$, where R=Al, Cr, Fe, and $R_4(W_{12}SiO_{40})$ $93H_2O$, where R=Al, Cr, Fe, Ga, In, crystallise in octahedra. Lastly, the salt K_3InCl_6

$1\frac{1}{2}H_2O$, which was first prepared by Meyer (6), and re-examined by Fock (7), was found to be isomorphous with K_3TlCl_6 $2H_2O$ and with $(NH_4)_3TlCl_6$ $2H_2O$, and mixed crystals were obtained by Fock of K_3InCl_6 $I\frac{1}{2}H_2O$ and K_3TlCl_6 $2H_2O$, the crystal constants of which closely resembled those of its components. Pratt (8) found that K_3TlBr_6 H_2O was isomorphous with the above three salts, so that the unusual case is here presented of salts of the same chemical type, but varying in the number of molecules of water of crystallisation, showing isomorphous relationships. In this connection Groth (9) remarks: 'The explanation of these remarkable relationships can naturally only be obtained by again completely and systematically examining these and all analogous compounds.'

So far then as the crystallography of the salts of indium has been determined, it is evident that the results show only indefinite isomorphous relationships between indium and a wide class of trivalent metals, including Fe, Cr, Al, Ga, and Tl, and do not point to any specially close relationship within the sub-group Ga, In, Tl. It seemed advisable to compare the crystallographical character of corresponding salts of thallium and indium in particular, especially as the work on the double sulphates had brought to light no isomorphous relationships between indium and thallium compounds. As the complex alkali halides gave promise of the best results, and as the work on these salts might at the same time lead to the elucidation of the unusual case of isomorphism referred to above, attention was confined to the chlorides and bromides of indium and thallium with K, NH_4, Rb, Cs, and Tl.

As already mentioned, the work of Rammelsberg (10) and Fock (7) on K_3TlCl_6 $2H_2O$, of Meyer and Groth (6), and of Fock (7), on K_3InCl_6 $1\frac{1}{2}H_2O$, of Rammelsberg (10) on $(NH_4)_3TlCl_6$ $2H_2O$, and of Pratt (8) on Rb_3TlBr_6 H_2O, seemed to indicate isomorphism in this rather remarkable group. Pratt also found that the salts Rb_2TlCl_5 H_2O and Cs_2TlCl_5 H_2O were isomorphous in the rhombic bipyramidal system, and Meyer (11) prepared

an indium salt which corresponded in formula to $(NH_4)_2InCl_5$ H_2O, but which he did not examine crystallographically. A review of previous work seemed then to indicate the possibility of obtaining two fairly long isomorphous series, of the types $R_3MX_6?H_2O$ and $R_2MX_5H_2O$ respectively, where R=K, NH_4, Rb, Cs, and possibly Tl; M=Tl, In; and X=Cl, Br. Still another series—of the type RMX_4 $?H_2O$—might prove of interest in this connection, more especially with X=Br or I. Nickles (12) obtained the salts $KTlBr_4$ $2H_2O$ and NH_4TlBr_4 $2H_2O$, and considered them to be rhombic, but gave no crystallographical details; while Pratt (8) found that the salts $RbTlBr_4$ H_2O and $CsTlBr_4$ crystallised in the cubic system. As part of the proposed investigation it was considered necessary to redetermine the crystallography of such members of isomorphous series as had already been investigated. A certain amount of the published data was too indefinite in detail to be made use of in an investigation on iosmorphism, where it is imperative that the data be the most accurate that can be obtained. It was also necessary to analyse the compounds of the type R_3MX_6 $?H_2O$, with reference especially to the amount of water which they contain. If the formulæ given for these salts is correct, it would seem that the water of crystallisation is in solid solution in the crystals, and does not play any fundamental part in determining the crystal structure.

Methods of Preparation and Analysis

The general method adopted for the preparation of the crystals was as follows. Thallic or indic oxide was dissolved in rather more than the requisite amount of halogen acid, and the alkali added in the proportion required by the formula. The salt was then allowed to crystallise on evaporating the solution either at room temperature or by gradual cooling in a crystallisation apparatus. As the salt sought for might be

in equilibrium at room temperature with a solution widely differing in composition from that represented by the formula of the salt, the concentration of the solution had to be varied till the required salt was found to crystallise. On dissolving thallous oxide in the halogen acid, any thallous ions present go to form insoluble thallous halide; consequently the difficulties which attend investigations on the thallic sulphates on account of the continuous reduction in the solution of thallic ions to thallous ions, were obviated here. So long as an excess of acid is present, practically no thallous ions can remain in solution. Excess of acid also prevents hydrolysis from taking place; in the case of the indium solutions, precipitation of the hydroxide was only prevented by maintaining the solutions decidedly acid, during the process of crystallisation.

The analyses were carried out as follows. After being carefully crushed, and dried at room temperature, the salt was gradually heated in a drying oven, and weighed at intervals, all precautions being taken to avoid overheating and consequent disintegration. On constant weight being attained, the water of crystallisation was estimated. The salt was dissolved in water, and the thallic or indic hydroxide precipitated by addition of ammonia. Meyer (13) found that only two-thirds of the chloride in a thallic chloride solution is precipitated by silver nitrate in strong nitric acid, a fact which points to the formation of complex ions in the solution. It is therefore necessary to remove the thallium or indium from the solution before estimating the halogen. Indium was estimated as In_2O_3, precautions being taken to ensure that no sublimation took place during the heating of the hydroxide. Thiel and Koelsch (2), on investigating this method of estimating indium, found that at a temperature of 850° C. no loss of weight took place through sublimation, while at 1000° C. the sublimation was considerable. Unless in the case where the solution contained a large amount of ammonium nitrate, it was found that

a temperature of 850° C. was sufficiently high to transform $In(OH)_3$ into In_2O_3. When, however, there is excess of NH_4NO_3, a certain amount of nitric oxide remains absorbed in the oxide at 850°. Here the amount of ammonia used for precipitating the hydroxide was the actual minimum sufficient to ensure complete precipitation, since indium hydroxide passes to some extent into colloidal solution in presence of much ammonia. Consequently there was small likelihood of error due to absorption of gas by In_2O_3; the hydroxide was, however, heated to 900°, to ensure the elimination of any residual gas. There was no evidence of sublimation at this temperature.

To estimate thallium, the precipitated thallic hydroxide was redissolved in sulphuric acid, and reduced to the thallous state by passing a current of sulphurous acid through the solution. This was then evaporated to dryness to drive off the last trace of sulphurous acid, and the thallium was now estimated by the bromine method (14). As any sulphurous acid in the solution would reduce the bromate and lead to too high a result for the thallium-content, it was essential that all traces of the gas be first removed. Although the bromine method involved some rather troublesome processes, it was, on the whole, more trustworthy than the peroxide method (1), since it took into account any thallium that might be reduced to the thallous state during the precipitation of the hydroxide.

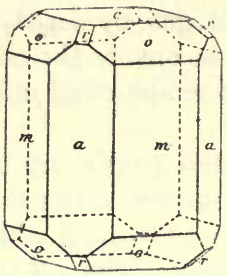
The solution from which the hydroxide had been precipitated was then acidified with nitric acid, and the halide was precipitated and estimated as silver halide. In the case of bromides excess of silver nitrate was added and the solution boiled. The excess of silver was then got rid of by addition of hydrochloric acid; the filtrate was evaporated to dryness with sulphuric acid, and the alkali metal estimated as sulphate.

Detailed Crystallography of the Various Salts

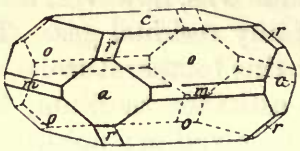
I: The series $R_3MX_6\ 2H_2O$

$K_3TlCl_6\ 2H_2O$

This salt crystallises equally well in two distinct habits, one of which has already been described by Fock (7). In the one case the crystals are elongated along the *c* axis (Fig. 1), and the prism faces {110} are well developed. The other



$K_3TlCl_6\ 2H_2O$ (*a*)
Fig. 1



$K_3TlCl_6\ 2H_2O$ (*b*)
Fig. 2

habit, which was not observed by Fock, is illustrated in Fig. 2. The crystals are here tabular on {001}, and the faces of {110} are reduced to very narrow bands. {101} is in all cases small, but was represented in all the crystals examined. {111} is well developed, and gives particularly good reflections.

The following are the crystallographical data :—

System : ditetragonal bipyramidal.

Axial constants : a : c=1 : ·7941.

Angle	No. of Measurements	Limits	Average	Calculated	Diff.	Fock	Rammelsberg
{001}:{111}	56	48° 9′—48°27′	48°19′			48°13′	48°30′
{001}:{101}	18	38°15′—38°36′	38°27′	38°27′	0′		
{111}:{111}	48	63°29′—63°54′	63°42′	63°45′	3′	63°38′	

Forms present : {100} {110} {001} {101} {111}.

S. G.=2·859 at 20°. Cleavage indistinct, // {100}.

Double refraction very weak. For this and other thallium salts, the refractive index is so high that no suitable liquid can be found of sufficiently high refractive index to be made use of in the total reflection method of measuring the double refraction. Consequently no refractive index data are given in this investigation.

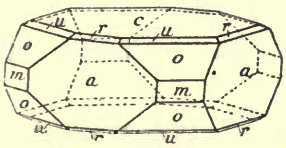
The following are the results of the analyses of the water of crystallisation :—

Average of Analyses	$K_3TlCl_6 2H_2O$	$K_3TlCl_6 1\frac{1}{2}H_2O$
H_2O 6·43 %	6·31 %	4·82 %

This salt undoubtedly crystallises with two molecules of water of crystallisation.

$(NH_4)_3TlCl_6$ $2H_2O$

This salt crystallises tabular on {001} (Fig. 3). Large, well-formed crystals were obtained, which in no case showed



$(NH_4)_3TlCl_6 2H_2O$

FIG. 3

indications of prismatic growth parallel to the *c* axis. The faces of {100} were well developed, while those of {110} were small. {111} was always represented, and {113} occurred as small faces giving quite good reflections. Faint indications of {103} were also observed, but the reflections were not good enough to give reliable measurements. The best reflections were obtained from the faces of {111}.

Rammelsberg (10) mentions the forms {100}, {110}, {101}, {111}, {001}, but he evidently found no indication of {113} or {103}.

System: Ditetragonal bipyramidal.

Axial constants: a : c = 1 : ·8097.

Angle	No. of Measurements	Limits	Average	Calculated	Diff.	Rammelsberg
{001} : {111}*	43	48°37′—49° 3′	48°52′			48°22′
{001} : {101}	17	38°44′—39°11′	39° 6′	39° 0′	6′	38°40′
{111} : {111}	34	64°12′—64°33′	64°22′	64°22′	0′	64° 2′
{001} : {113}	5	20°29′—21°29′	21° 9′	20°54′	15′	

Forms present: {100}, {110}, {101}, {111}, {001}, {113}, with indications of {103}.

Cleavage very poor, // {100}.

S. G. = 2·389 at 20°.

It will be observed that the crystallographical details differ somewhat widely from the value given by Rammelsberg. Rammelsberg gave no details with regard to his measurements, which were made some thirty years ago, and would consequently require in any case to be revised to-day.

The estimations of the water of crystallisation gave the following results:—

Average of Analyses	$(NH_4)_3TlCl_6 2H_2O$	$(NH_4)_3TlCl_6 1\frac{1}{2}H_2O$
H_2O 7·15 %	7·11 %	5·43 %

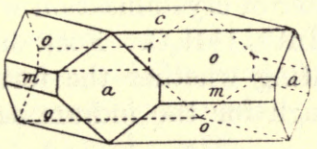
Considerable caution had to be exercised in heating this salt. At temperatures above 150° dissociation took place, the salt losing continuously in weight. Heating was continued at a temperature slightly under 150° until a practically constant weight was reached, and presumably the whole of the water of crystallisation had been liberated. The ammonium salt, like the potassium salt, crystallises with two molecules of water.

$K_3InCl_6\ 2H_2O$

This salt had been obtained by Meyer (6), and examined

crystallographically by Groth. Fock (7) re-examined the salt, and both Meyer and Fock gave the formula as $K_3InCl_6\ 1\frac{1}{2}H_2O$.

The salt is very soluble in water, and forms small, slightly yellowish crystals. From solutions containing potassium chloride and $InCl_3$ in the proportions 3 : 1, potassium chloride was precipitated on evaporation at room temperature till very little solution remained. Precipitation of the complex salt then took place in a solution in which the concentration of indium ions was very high. The crystals were either tabular on {001} (Fig. 4), or elongated along the C axis, and



$K_3InCl_6\ 2H_2O$
FIG. 4

showed large faces of {111}. On only one of all the crystals examined did the form {101} appear, and in that case it was very poorly developed. The faces of {100} were more pronounced than those of {110}, and the reflections were very good.

System : Ditetragonal bipyramidal.

Axial constants : a : c=1 : ·8173.

Angle	No. of Measurements	Limits	Average	Calculated	Diff.	Fock	Groth
{001} : {111}*	47	48°55′—49°25′	49° 8′			49°11′	49°13′
{111} : {111}	46	64°15′—64°52′	64°40′	64°40′	0′	64°47′	
{001} : {101}	1		39°15′	39°15′	0′		

Forms present: {100}, {110}, {001}, {111}, {101} on one crystal.

S. G.=2·483 at 20°.

The analyses gave the following results :—

	H_2O	K.	In.	Cl.
	6·87 %	25·00 %	23·26 %	43·92 %
Calculated for K_3InCl_6 $2H_2O$	7·50 %	24·40 %	23·87 %	44·24 %
„ „ K_3InCl_6 $1\frac{1}{2}H_2O$	5·74 %	24·86 %	24·04 %	45·25 %

With the exception of the potassium value, which is necessarily, owing to the method of analysis, less reliable than the other values, the averages all distinctly favour the formula K_3InCl_6 $2H_2O$. There is in this case no possibility of dissociation at temperatures between 150° and 200°, so that the values obtained for the water of crystallisation would be abnormally high for the salt K_3InCl_6 $1\frac{1}{2}H_2O$. Fock directed his attention mainly to investigating whether the formula K_3TlCl_6 $2H_2O$ was correct; although for the indium salt he obtained the analysis

	H_2O	Cl.	In.
	5·52	45·25	23·23
Calculated	5·74	45·25	24·04

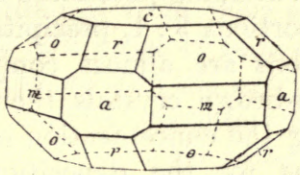
it seems probable that the salt was not heated sufficiently to drive off the last traces of the water of crystallisation, which is liberated at a temperature considerably above 150°. At any rate, it seems conclusively proved that this salt contains two molecules of water, and consequently agrees in formula with the two salts already described, with which it is isomorphous.

Rb_3TlBr_6 $2H_2O$

From solutions in which the relative proportions of RbBr and $InBr_3$ were those represented by the above formula, there were deposited on evaporation cubic crystals of $RbTlBr_4$ H_2O, and on further evaporation these were replaced by tetragonal crystals of Rb_3TlBr_6 $2H_2O$. This salt crystallises in honey-yellow crystals, developed on {001}, but not so pronouncedly tabular as in the case of $(NH_4)_3TlCl_6$ $2H_2O$ (Fig. 5). The faces

of {111} and {101} are well developed; and {110} occurs as fairly broad faces. The reflections are very good.

Pratt (8) described this salt as crystallising in the tetragonal system, but with only one molecule of water of crystallisation.



$Rb_3TlBr_6\ 2H_2O$

FIG. 5

The results of his investigations are given in a separate column in the following statement of the crystallography of the salt.

System: Ditetragonal bipyramidal.

Axial constants: a : c = 1 : ·8038.

Angle	No. of Measurements	Limits	Average	Calculated	Diff.	Pratt
{111} : {101}	44	31°57′—32°15′	32° 6′			32° 8½′
{101} : {001}	12	38°46′—38°56′	38°53′	38°48′	5′	38°54½′
{001} : {111}	10	48°44′—48°48′	48°46′	48°40′	6′	48°53′
{110} : {101}	28	63°26′—63°47′	63°40′	63°40′	0′	
{1$\bar{1}$1} : {011}	6	79°20′—79°54′	79°36′	79°30′	6′	

Forms present: {100}, {110}, {001}, {101}, {111}.

S. G.—4·077 at 20°.

The following are the results of analysis:—

	Rb.	Tl.	Br.	H_2O
	25·69	20·46	48·85	3·60
Calculated for $Rb_3TlBr_6 2H_2O$	26·25	20·90	49·15	3·69
„ „ $Rb_3TlBr_6\ H_2O$	26·76	21·30	50·06	1·88

The analysis shows that the salt crystallises with two molecules of water. All the water of crystallisation is driven off by heating the salt to 120° C., and it is rather difficult to

account for the low value for the water of crystallisation obtained by Pratt.

$K_3InBr_6\ 2H_2O$

From solutions containing potassium bromide and indium bromide in the proportions 3 : 1, precipitation of KBr takes place till the solutions are almost completely evaporated. Very small reddish-brown crystals then begin to appear. Although on varying the concentration of the solution more favourable conditions for the deposition of this salt are obtained, it crystallised invariably as a very fine powder, and good crystals could not be isolated. The angular measurements obtained in the goniometer showed that the crystals were isomorphous with the compounds already described. This salt effloresces, however, so readily on exposure to the air that it was found impossible to obtain exact crystallographical data. The specific gravity of the crystalline powder was found to be—as accurately as possible under the circumstances—3·140 at 20°.

Analyses gave the following results :—

	K.	In.	Br.
	16·89	15·24	63·97
Calculated	15·90	15·56	65·00.

Owing to the very efflorescent character of the salt, no attempt was made to obtain the value of the water of crystallisation. The salt is, however, undoubtedly isomorphous with compounds of the type $R_3MX_6\ 2H_2O$, and one is justified in assuming that it also contains two molecules of water of crystallisation.

No other salt isomorphous with those already described has been obtained in this investigation. It would appear that the only compounds of the series $R_3MX_6\ 2H_2O$, where R=K, (NH_4), Rb, Cs or Tl; M=In or Tl; X=Cl or Br, that are in equilibrium with their solutions under ordinary conditions of temperature and pressure are (1) $K_2TlCl_6\ 2H_2O$; (2) $(NH_4)_3$

$TlCl_6\ 2H_2O$; (3) $Rb_3TlBr_6\ 2H_2O$; (4) $K_3InCl_6\ 2H_2O$; and (5) $K_3InBr_6\ 2H_2O$. It is rather remarkable that while $Rb_3TlBr_6\ 2H_2O$ has been isolated, neither $K_3TlBr_6\ 2H_2O$ and $(NH_4)_3TlBr_6\ 2H_2O$ on the one hand, nor $Cs_3TlBr_6\ 2H_2O$ on the other, can be obtained from their solutions. Although the order of stability in a series of salts of similar formula—dependent as it is in the main on the varying solubilities of the different salts which may be precipitated—seems as a rule to have a definite relationship to the order of atomic weights, there are evidently markedly exceptional cases.

II: The series $R_2MX_5\ H_2O$

Crystallographical data have already been published on two salts belonging to this series, *i.e.* on $Rb_2TlCl_5\ H_2O$ and $Cs_2TlCl_5\ H_2O$ (see Pratt, *loc. cit.*). An isomorphous salt where X=Fe has been examined by Johnson(15)—namely $(NH_4)_2FeCl_5\ H_2O$. In the investigation of this series it was found that the crystals should be placed in a different position from that adopted by Pratt and Johnson, and it may be well to explain here why an interchange of the crystallographical axes has been made. The crystal system of the isomorphous series is rhombic bipyramidal, but there is a close resemblance to tetragonal habit. In the case of $Cs_2InCl_5\ H_2O$, for instance, the relative values of the crystallographical axes are ·9841 : 1. Unless there were some valid objection, the third axis, which differs markedly from these two, would be taken as the *c* axis, and the two specified axes as the *a* and *b* axes respectively. Now, on examining the crystals of $Rb_2InCl_5\ H_2O$, it was found that practically every individual was twinned on the unit prism face between the two almost equal axes as twinning plane, so that the twinned individual was turned almost through a right angle round the axis parallel to the prism face, thus accentuating the pseudo-tetragonal symmetry. It was

therefore decided to take this prism face as {110}, and the shorter of the two almost equal axes as the axis *a*. This prism had been formerly taken to be {101}; so that the new position of the crystal simply involved an interchange of the *b* and *c* axes, the *a* axis remaining as before; the change necessitated, in other words, a rotation of the crystal through 90° round the *a* axis. In the various crystals of the series there is a pronounced cleavage parallel to {011}, which has the same indices for both positions of the crystal. There is then no *a priori* reason, from cleavage considerations, why the crystal should have been placed in a position which tends to hide, rather than accentuate, its pronounced pseudo-tetragonal character.

$Rb_2TlCl_5\ H_2O$

From the solution containing the chlorides RbCl and $TlCl_3$ in the proportion given in the salt formula, thin flakes of $Rb_3TlCl_6\ H_2O$ (monoclinic) are first precipitated. On further evaporation these disappear, being replaced by large well-formed crystals of $Rb_2TlCl_5\ H_2O$. These crystals are much distorted, being always tabular on {101}, the faces of which are extremely well developed. Truncating the edges of the pinacoid formed by two large faces of {101} are three smaller faces on the upper side, and three on the lower side of the crystal plate. These are the two remaining faces of {101}, and the four faces of {001}. Were it not for the pronouncedly tabular habit, the combination of the two forms {101} and 011} would strongly suggest the octahedron; as it is, each crystal appears as a triangular plate with the vertices cut away. The characteristic habit of the crystal is shown in Fig. 6. The faces of {100} occur very seldom, and are then represented by narrow threadlike bands. The reflections are very good.

The interfacial angular measurements of Pratt are appended to the following table of crystallographical data :—

Crystal system: Rhombic bipyramidal.

Axial constants: a : b : c = ·9770 : 1 : 1·4386.

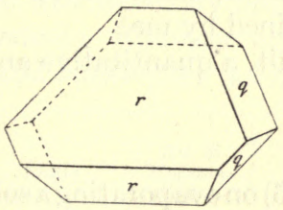
Angle	No. of Measurements	Limits	Average	Calculated	Diff.	Pratt
{011}:{01$\bar{1}$}	11	69°31′—69°41′	69°36′			69°36′
{011}:{101}	52	70°55′—71°35′	71°18′			71°24½′
{101}:{$\bar{1}$01}	12	67°58′—68°40′	68°20′	68°22′	2′	68° 7½′
{100}:{120}						62°52½′
{011}:{120}						63°19′

Forms present: {011}, {101}. {100} occurs seldom and very poorly developed.

{120} not found, though observed by Pratt.

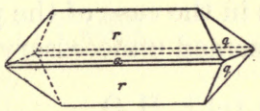
S. G. = 3·513 at 20°.

No analyses were made in the case of this salt, as there was no question as to its identity, and sufficiently full analyses had already been made by Pratt to establish its formula.



$Rb_2TlCl_5\ H_2O$

FIG. 6



$Cs_2TlCl_5\ H_2O$

FIG. 7

$Cs_2TlCl_5\ H_2O$

The solution contained CsTl and $TlCl_3$ in the proportion 2 : 1. There crystallised on evaporation large hexagonal plates of $Cs_3Tl_2Cl_9$, and these gradually gave place to prisms of $Cs_2TlCl_5\ H_2O$. This salt is sparingly soluble in water, and crystals 5—6 mms. long were frequently obtained. The larger crystals were usually opaque. They are elongated along the *b* axis, with well-developed faces of {101} (Fig. 7). The end

faces are comparatively small, but give good reflections, whereas the faces of {101} are badly striated. {100} occurs, but the faces are narrow and very poorly developed. {120} was not found on any crystal examined.

Crystal system: Rhombic bipyramidal.

Axial constants: a : b :c=·9690 : 1 : 1·4321.

Angle	No. of Measurements	Limits	Average	Calculated	Diff.	Pratt
{011}:{01$\bar{1}$}*	18	69°17′—70° 9′	69°51′			70° 0′
{011}:{101}*	24	70°54′—71°30′	71°17′			71°15′
{101}:{$\bar{1}$01}	23	67°59′—68°38′	68° 9′	68°10′	1′	68°22′
{100}:{120}						62°51′
{011}:{120}						43° 9′

S. G.=3·879 at 20°.

Forms present: {011}, {101}, {100}.

Here, too, Pratt observed the form {120} on some of the crystals he examined, although the form did not occur on the crystals from any of the crops examined by me.

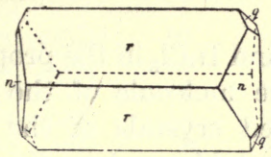
As in the case of the preceding salt, a quantitative analysis was deemed unnecessary here.

$(NH_4)_2InCl_5\ H_2O$

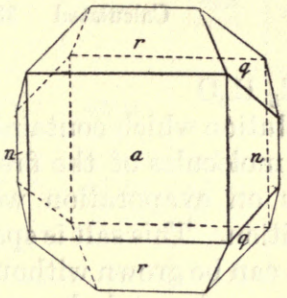
This salt was obtained by Meyer(16) on evaporating a solution containing $(NH_4)Cl$ and $InCl_3$, in his attempt to isolate a compound similar to $K_3InCl_6\ 1\frac{1}{2}H_2O$. He mentioned that the crystals seemed different in form from those of the potassium salt, but evidently no detailed examination was made.

The habit of the crystals seems to vary with the composition of the original solution. From a solution where the proportion of the NH_4 ions to the In ions was that represented by the formula $(NH_4)_3InCl_6\ 2H_2O$, crystals of $(NH_4)_2InCl_5\ H_2O$ were precipitated which were elongated along the *b* axis, had well-developed faces of {101}, fairly good faces of {120},

and small faces of {011} (Fig. 8). From solutions, however, where the relative proportions of the metallic ions were those represented by $(NH_4)_2InCl_5\ H_2O$, the crystals always showed large faces of {100}. Such crystals were either developed along



$(NH_4)_2InCl_5\ H_2O(a)$
FIG. 8



$(NH_4)_2InCl_5\ H_2O$ (*b*)
FIG. 9

the *c* axis, and carried fairly large faces of {120}, or were tabular on {100} (Fig. 9). {101} was always well represented. The crystals were slightly yellowish, and the cleavage parallel to {011} was especially pronounced.

System: Rhombic bipyramidal.

Axial constants: a : b : c = ·9663 : 1 : 1·4005.

Angle	No. of Measurements	Limits	Average	Calculated	Diff.
{101} : {$\bar{1}$01}*	22	69° 6′—69°18′	69°13′		
{101} : {120}*	36	67°40′—68° 5′	67°47′		
{120} : {$\bar{1}$20}	16	54° 1′—55° 2′	54°38′	54°42′	4′
{011} : {01$\bar{1}$}	20	70°14′—71° 0′	70°49′	71° 2′	13′
{120} : {011}	24	43° 8′—43°48′	43°33′	43°42′	9′
{101} : {011}	16	70°10′—71° 4′	70°43′	70°43′	0′

Forms present (on both types of crystal habit): {101}, {120}, {011}, {100}.

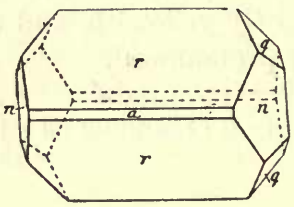
S. G. = 2·281 at 20°.

The crystals give up their water of crystallisation very slowly on heating. The analyses of the salt gave the following result :—

	In.	Cl.	H_2O
	32·70	49·63	5·30
Calculated	33·19	51·21	5·20.

$Rb_2InCl_5\ H_2O$

A solution which contains RbCl and $InCl_3$ in the proportion of two molecules of the first to one molecule of the second deposits on evaporation well-formed crystals of the above composition. This salt is sparingly soluble, and medium-sized crystals can be grown without difficulty. In habit the crystals are more or less tabular on {101}, and are usually elongated along the *b* axis. They show large faces of {101}, and fairly well-developed faces of {120}; {011} and {100} are small, but are represented on all the crystals investigated. The general



$Rb_2InCl_5\ H_2O$
FIG. 10

habit is shown in Fig. 10. The reflections are good from all faces except from those of {101}, which frequently give multiple reflections. Dispersion is high. Practically all the crystals are twinned, the twinning plane being {110}; the two individuals of the interpenetrating twin cross at an angle of 88° 22′. The interpenetrating twin, looked at from above, bears a marked resemblance to the iron cross of pyrites, the {120} faces of the second individual appearing through the large faces of {101} on the first.

The crystallographical data are as follows :—

System : Rhombic bipyramidal.

Axial constants : a : b : c = ·9725 : 1 : 1·4065.

Angle	No of Measurements	Limits	Average	Calculated	Diff.
{101} : {10$\bar{1}$}*	27	68°49′—69°37′	69°15′		
{120} : {$\bar{1}$20}*	63	53°59′—54°45′	54°25′		
{011} : {0$\bar{1}$1}	16	70°26′—71° 8′	70°47′	70°45′	2′
{120} : {011}	11	43°16′—43°53′	43°32′	43°31′	1′
{101} : {120}	8	67°43′—68° 1′	67°46′	67°54′	8′
{101} : {011}	14	70°34′—71°14′	70°50′	70°48′	2′

Forms present : {100}, {101}, {120}, {011}.

Twinning on {110}.

S. G. = 3·037 at 20°.

The analyses of the carefully dried powder gave the following results :—

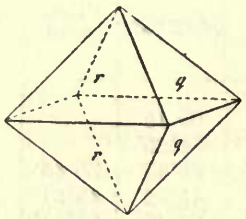
	Rb.	In.	Cl.	H_2O
	35·01	23·92	35·32	1·46
Calculated	35·52	23·86	36·87	2·75.

The values for chlorine and for water are both low. The water of crystallisation is held firmly in this salt, and is probably not entirely driven off even at 200°. For some reason not fully understood, the method of analysis adopted for this series of isomorphous salts gave consistently low results for the halogen.

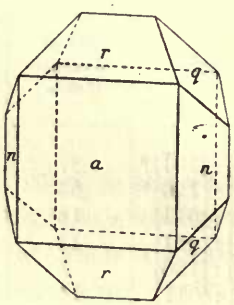
$Cs_2InCl_5\ H_2O$

The crystals of this salt, which were obtained on allowing a solution which contained CsCl and $InCl_3$ in the proportion 2 : 1 to evaporate at laboratory temperatures, were very simple in type. They represented a combination of the two forms {101} and {011}, usually equally developed (Fig. 11), so that the crystals appeared cubic, developed on {111}.

Occasionally there was a tabular development on {101}. On only one crystal was the form {100} found. No cases of twinning were observed.



$Cs_2InCl_5\,H_2O$
FIG. 11



$(NH_4)_2InBr_5\,H_2O$
FIG. 12

The crystals were colourless, and relatively insoluble in water. They were as a rule small, badly formed, and gave multiple, indefinite reflections. From the various crops which were grown, it was found difficult to obtain a sufficiently large number of crystals capable of yielding fairly reliable results. The crystals of this salt are distinctly poorer than those of any other member of the series.

System: Rhombic bipyramidal.

Axial constants: a : b : c = ·9841 : 1 : 1·4033.

Angle	No. of Measurements	Limits	Average	Calculated	Diff.
{011} : {01$\bar{1}$}*	14	70°45′—71°12′	70°57′		
{101} : {011}*	30	70°20′—70°44′	70°32′		
{101} : {10$\bar{1}$}	5	69°44′—70°0′	69°56′	70°5′	11′

Forms present: {101}, {011}.
{100} on one crystal.

S. G. = 3·350 at 20°.

Analyses gave the following results :—

	Cs.	In.	Cl.	H_2O
	45·62	20·43	30·09	3·27
Calculated	46·13	19·94	30·80	3·13.

$(NH_4)_2InBr_5\ H_2O$

From a solution containing NH_4Br and $InBr_3$ in the proportions of two to one, a fine-grained crystalline powder was precipitated, brownish in colour and very soluble in water. The crystals proved to be very deliquescent, and no exact crystallographical measurements could be made. The habit of the crystals is illustrated in Fig. 12. They are elongated along the *c* axis, slightly tabular on the well-developed faces of {100}, and show fairly large faces of {120}, {101}, and {011}. The specific gravity is, as accurately as could be measured under the circumstances, 3·167 at 20°.

Analyses gave the following results :—

	In.	Br.	H_2O
	19·70	70·11	5·92
Calculated	19·73	70·30	6·48.

After standing in the solution for four days, the crystals became quite opaque. The slightest changes of temperature seem to affect the stability of this salt when in contact with the solution at ordinary room temperatures.

$Rb_2InBr_5\ H_2O$

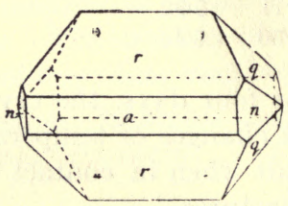
From solutions in which RbBr and $InBr_3$ are in the proportions respectively of 1 : 1 or 2 : 1, crystals of the above salt are formed at room temperatures. The crystals are colourless, fairly insoluble, and are frequently rather cloudy. They are usually developed along the *b* axis, show broad faces of {100}, large faces of {101}, and comparatively small faces of {120} and {011} (Fig. 13).

The following are the crystallographical data :—
System : Rhombic bipyramidal.
Axial constants : a : b : c :=·9803 : 1 : 1·3951.

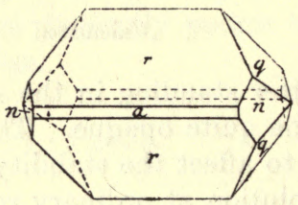
Angle	No. of Measurements	Limits	Average	Calculated	Diff.
{101} : {011}*	24	69°59′—70°48′	70°26′		
{0$\bar{1}$1} : {011}*	16	70°49′—71°42′	71°16′		
{101} : {$\bar{1}$01}	18	69°26′—70° 5′	70° 1′	70°11′	10′
{120} : {011}	3	43°39′—43°51′	43°44′	43°37′	7′
{120} : {101}	9	67°28′—68°30′	67°50′	68°10′	20′
{120} : {1$\bar{2}$0}			54° 3′		

Forms present : {100}, {120}, {101}, {011}.
S. G.=3·409 at 20°.
The results of the analyses are as follows :—

	Rb.	In.	Br.	H_2O
	23·10	16·67	56·18	3·25
Calculated	24·29	16·64	56·32	2·61



$Rb_2InBr_5\ H_2O$
FIG. 13



$Cs_2InBr_5\ H_2O$
FIG. 14

$Cs_2InBr_5\ H_2O$

From solutions which contained CsBr and $InBr_3$ in the proportion 2 : 1, crystals of this salt were very easily obtained on evaporation. They are very insoluble, colourless, and markedly lustrous. The crystals are small and well formed, and give good reflections. No evidence of twinning was found. The general habit of the crystals somewhat resembles that described for $Rb_2InBr_5\ H_2O$ (Fig. 14). There is a marked

elongation along the *b* axis: {100} is here very small, while {101} is particularly well developed. {011} has fairly good faces, but {120} was found on only one of the crystals examined.

The following are the crystal measurements:—

System: Rhombic bipyramidal.

Axial constants: a : b : c = ·9734 : 1 : 1·4180.

Angle	No. of Measurements	Limits	Average	Calculated	Diff.
{101} : {011}*	35	70° 35′—71°10′	70°58′		
{011} : {01$\bar{1}$}*	21	{70°}14′—70°43′	70°23′		
{101} : {10$\bar{1}$}	11	68° 29′—69° 4′	63°45′	68°55′	10′
{120} : {$\bar{1}$20}				54°23′	
{120} : {011}	2	43° 16′—43°38′	43°27′	43°22′	5′

Forms present: {100}, {101}, {011}: {120} occurs only once.

S. G. = 3·776 at 20°.

Analyses give the following results:—

	Cs.	In.	Br.	H_2O
	32·80	14·45	49·42	2·47
Calculated	33·30	14·38	50·07	3·26.

III: The Series $RMx_4\ xH_2O$

From the point of view of the present investigation this series is relatively unimportant, as each member of the series crystallises in the cubic system. The crystallographical values are therefore identical, and, as the values for the refractive indices could not be obtained for the thallium salts, there was nothing to indicate the change in crystalline structure due to the replacement of one element by another. Consequently no thorough investigation was made of the salts belonging to this series. Nickles (12) stated thatthe two salts of the composition $KTlBr_4\ 2H_2O$ and $NH_4TlBr_4\ 2H_2O$ are isomorphous, crystallising in the rhombic system; and Meyer (17) also refers to the former of these two salts as rhombic. Pratt (8)

has described $RbTlBr_4\ H_2O$ and $CsTlBr_4$ as crystallising in cubes. These salts were all obtained in this investigation, but the crystalline form of $KTlBr_4\ 2H_2O$ and $NH_4TlBr_4\ 2H_2O$ was found to be cubic, not rhombic. The crystals were tabular, showing only the face of {100}, with depressions in the form of inverted rectangular pyramids. Under the microscope the crystals were perfectly isotropic in all positions.

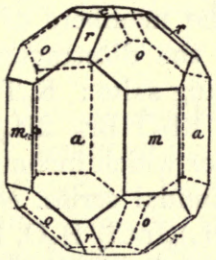
No corresponding indium bromides were obtained, and no thallium or indium chloride of this general type was isolated. From solutions, however, which contained KBr and $TlBr_3$ in the proportion 3 : 1, a salt was obtained, which, although not belonging to this series, may be described here. This salt was deposited in beautiful yellowish brown crystals of high lustre from solutions which had previously precipitated cubic crystals of $KTlBr_4\ 2H_2O$.

$K_3Tl_2Br_9\ 3H_2O$

Rammelsberg (18) had obtained a salt of this composition from solutions containing TlBr, Br, KBr, and water. He described the crystals as yellowish and apparently regular, showing the faces of {111}, {100}, and {110}. Meyer (13) failed to obtain this salt, and considered that the salt which Rammelsberg obtained was probably $KTlBr_4\ 2H_2O$. I succeeded in obtaining both salts, crystallising together from various solutions of the composition $K_3Tl_2Br_9\ xH_2O$. The stability conditions of the salt under consideration were not fully made out. Whenever it appeared, it crystallised subsequent to the precipitation of $KTlBr_4\ 2H_2O$, and the slightly reddish tinge of the crystals made them conspicuous among the pale yellow plates of the other salt. But in many cases—usually on slight rise of room temperature—the crystals disappeared shortly after formation; and from several solutions no precipitation of the salt took place. Low room-temperatures and fairly acid solutions were distinctly favourable conditions.

When formed under the most suitable conditions, the crystals possessed a markedly high lustre; but usually the lustre was dull and the reflections poor. This may probably be accounted for by the fact that at temperatures above the average room temperature, efflorescence was observed to take place.

Fig. 15 shows the general habit of the crystals. They belong to the ditetragonal bipyramidal class, and are usually



$K_3Tl_2Br_9\ 2H_2O$
FIG. 15

slightly elongated along the *c* axis. The form {100} is well developed, as is also the form {111}. {110} is less pronounced, and {101} very small, occurring in only a few crystals. The crystals are capped by small faces of {001}. Under suitable conditions of growth, large well-formed crystals were always obtained.

System: Ditetragonal bipyramidal.

Axial constants: a : c=1 : ·7556.

Angle	No. of Measurements	Limits	Average	Calculated	Diff.
{010}:{111}*	46	58°38′—59° 3′	58°55′		
{110}:{111}	24	43° —43°25′	43°12′	43° 6′	6′
{110}:{011}	8	64°42′—65°12′	64°49′	64°46′	3′
?	4	76°10′—76°24′	76°17′		

Forms present: {001}, {100}, {110}, {111}, {101}.

The analyses gave the following results :—

	K.	Tl.	Br.	H_2O
	8·46	31·74	55·05	4·75
		(diff.)		
Calculated	9·03	31·42	55·30	4·16.

Comparison of Data

Full crystallographical details have been given in the foregoing section for the members of two distinct series of isomorphous salts—(1) the ditetragonal bipyramidal series, consisting of the following salts: K_3TlCl_6 $2H_2O$, $(NH_4)_3TlCl_6$ $2H_2O$, K_3InCl_6 $2H_2O$, Rb_3TlBr_6 $2H_2O$, to which may be added K_3InBr_6 $2H_2O$, for which incomplete details are given ; (2) the rhombic bipyramidal series, consisting of: Rb_2TlCl_5 H_2O, Cs_2TlCl_5 H_2O, $(NH_4)_2InCl_5$ H_2O, Rb_2InCl_5 H_2O, Cs_2InCl_5 H_2O, Rb_2InBr_5 H_2O, Cs_2InBr_5 H_2O, to which may be added $(NH_4)_2InBr_5$ H_2O, for which incomplete details were obtained. On referring to the literature it would appear that only one other salt has been described which shows any marked similarity in its crystallography to the members of the first series, *i.e.*, $K_3SbCl_3Br_3$ $1\frac{1}{2}H_2O$. This salt was obtained by Atkinson and described by Solly (19), who gave the following details :—

Class : Tetragonal bipyramidal.

Crystal constants : a : c=1 : ·7629.

Angle	Calculated	Observed
$\{111\}:\{1\bar{1}1\}$*		62°29′
$\{111\}:\{11\bar{1}\}$	85°39′	85°40′

Forms : {111}, with occasionally small faces of {001}.

Although the estimated water value differs by half a molecule from that given for the isomorphous series, and the

crystals are markedly poorer in faces, the general similarity of chemical composition, and of angular values, justifies the inclusion of this salt in the isomorphous series. In comparing this salt with the others of the series, the values already quoted will be used.

Isomorphous with the second series are two salts, $K_2FeCl_5 H_2O$ and $(NH_4)_3FeCl_5 H_2O$. The former is the mineral Erythrosiderite (20), for which the crystal constants are (adopting the same placing of the crystal as in the isomorphous series) a : b : c :=·9628 : 1 : 1·3931, and in which the combination {101}, {011}, {100}, and {120} occurs: on crystals formed in the laboratory the octehedral-like combination of {101} and {011}, similar to that already described for $Cs_2InCl_5 H_2O$, is characteristic. The salt $(NH_4)_2FeCl_5 H_2O$ has been described by Johnson (15). He found that the forms {101} and {011} predominate, {100} is sometimes large, and {120} small. Two twinning laws were observed—(1) twinning axis perpendicular to {111}; (2) twinning plane {110}.

System: Rhombic bipyramidal.

Axial constants: a : b : c=·9749 : 1 : 1·4239.

Angle	Calculated	Observed
{101} : {10$\bar{1}$}*		68°48′
{100} : {120}*		62°51′
{011} : {01$\bar{1}$}	70°10′	70°17′
{011} : {120}	43°16′	43°10′
{011} : {101}	71° 3′	71°11′
{101} : {120}	68°28′	68°30′

S. G.=1·99.

These two compounds of iron are the only salts hitherto described which are undoubtedly isomorphous with the series of indium and thallium salts under discussion. The crystallography, as quoted above, will be used when comparison is made between the various members of the series.

Within the limits of the present contribution it is impossible to enter into a full discussion of the practical results here described; that must be reserved for subsequent publication elsewhere. Some general conclusions drawn from a detailed comparison of the various salts which have been examined is given, however, in the summary which follows.

SUMMARY

1. The ditetragonal bipyramidal series, consisting of the salts (*a*) $K_2TlCl_5\,2H_2O$, (*b*) $(NH_4)_2TlCl_5\,2H_2O$, (*c*) $K_2InCl_5\,2H_2O$, (*d*) $Rb_2TlBr_5\,2H_2O$, (*e*) $K_2InBr_5\,2H_2O$, was investigated, and full crystallographical details are given for all the salts except $K_2InBr_5\,2H_2O$, which effloresces so readily that exact measurements are impossible. It had formerly been considered that $K_2TlCl_5\,2H_2O$, $(NH_4)_2TlCl_5\,2H_2O$, $K_2InCl_5\,1\frac{1}{2}H_2O$, and $Rb_2TlBr_5\,H_2O$ were isomorphous. The investigation has shown that all the salts of this isomorphous series have two molecules of water of crystallisation.

2. The rhombic bipyramidal series, consisting of the salts (*a*) $Rb_2TlCl_5\,H_2O$, (*b*) $Cs_2TlCl_5\,H_2O$, (*c*) $(NH_4)_2InCl_5\,H_2O$, (*d*) $Rb_2InCl_5\,H_2O$, (*e*) $Cs_2InCl_5\,H_2O$, (*f*) $(NH_4)_2InBr_5\,H_2O$, (*g*) $Rb_2InBr_5\,H_2O$, (*h*) $Cs_2InBr_5\,H_2O$, was investigated. Of these, the indium salts—with the possible exception of $(NH_4)_2InCl_5\,H_2O$—were prepared for the first time, and quantitative analyses are appended. The series is isomorphous, and crystallographical details are given in full, except in the case of $(NH_4)_2InBr_5\,H_2O$, which is very deliquescent.

3. The following salts were found to crystallise in cubes in the regular system:—$KTlBr_4\,2H_2O$, $(NH_4)TlBr_4\,2H_2O$, $RbTlBr_4\,H_2O$, and $CsTlBr_4$. Of these the first two had formerly been taken as rhombic.

   Details of the crystallography of the salt $K_3Tl_2Br_9\,3H_2O$, which crystallises in the ditetragonal bipyramidal class, are also appended.

4. The results of the investigation on the isomorphous relationships in the above-mentioned series, and the additional salts $K_2FeCl_5\,H_2O$ and $(NH_4)_2FeCl_5\,H_2O$ (which are isomorphous with the second series), may be summarised as follows:—

   (*a*) Crystal Habit—

   The alkalies stand in the following order:—NH_4, Rb, Cs. Cl and Br are very closely related. The salts of Fe, In, Tl differ widely from each other.

(*b*) Interfacial Angles—

For the alkalies the order is:—Rb, NH_4, Cs, with NH_4 very near Rb. The interval Cl—Br is of the same order of magnitude as the interval Rb—Cs. The greatest change in interfacial angles is obtained by replacement within the group Fe, In, Tl; the effect is roughly proportional to the change in atomic weight. The effect of the replacement In > Tl is opposite in sense to that of NH_4 > Cs, Cl > Br, Fe > In, or Rb > NH_4.

(*c*) Molecular Volumes, Axial Constants, and Molecular Distance Ratios—

In regard to molecular volume and molecular distance ratios, the alkalies stand in the following order:—K, NH_4, Rb, Cs, with NH_4 near to Rb. Replacement affects mainly the χ and ψ values. Substitution of Br for Cl causes an especially large extension along the three axial directions, a fact which probably indicates a symmetrical disposition of the halogen atoms in the molecule. Within the group Fe, In, Tl, replacement has only a small effect on the molecular volume and molecular distance ratios, the effect being seen mainly in the ω value. In and Tl are more closely related than are Fe and In.

The axial constants afford no definite results in this connection.

5. In the complex salts of indium and thallium under consideration, the greater the atomic weight of the alkali, the less is the amount of water in the salt. The greater the atomic weight of the alkali, the less also is the ratio $RX : MX_3$ in the chemical constitution of the salt. The ratio $RX : MX_3$ is, speaking generally, lower in the indium chlorides than in the corresponding thallium chlorides, and in the thallium bromides than in the corresponding indium bromides. The relative concentrations of complex ions in the thallium and indium solutions are important factors in determining the stability of the various salts.

I have to acknowledge my deep indebtedness to Professor Hugh Marshall, of University College, Dundee, in whose laboratory the experimental part of this investigation was carried out, for his valuable advice and for his great interest in the work.

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ROBERT CHARLES WALLACE

NATURAL HISTORY AND MEDICINE

A BRIEF HISTORY OF THE CHAIR OF NATURAL HISTORY AT SAINT ANDREWS

With a somewhat hostile neighbour south of the Tweed, and a recollection, according to Cosmo Innes, that northern students were not popular, and even that they were molested at Oxford,[1] it was no wonder that Bishop Wardlaw's efforts to found the University of St Andrews were cordially seconded by his King and his countrymen; nor that with the friendly relations then existing between France and the independent Scots the University was, in 1411, modelled on the plan of that of Paris, even to the shape of the gowns. But though the power of granting degrees in medicine and law dates from a very early period in the history of the University, Natural History, and indeed all the natural and physical sciences, found no place amongst the subjects originally taught. Theology and the lines which led up to it, viz. Greek, Latin (*Literæ Humaniores* as they were called), Logic, Philosophy, Metaphysics, Grammar, Poetry, and Oratory alone received attention in the three colleges of St Andrews. In other words, the purely classical, clerical, and literary subjects for the most part held the foremost place for many generations. Nor was this remarkable when it is remembered that it was to the wise foresight, influence, and energy of the early ecclesiastical scholars that the universities, and more especially that of St. Andrews, came into existence.

Passing, therefore, a period of nearly three hundred years, the story of which does not immediately concern the present

[1] *Story of the University of Edinburgh*, Sir A. Grant, vol. i. pp. 1 and 3.

subject, the date of the union of the colleges of St Salvator and St Leonards is reached. In carrying out the scheme for the United College about the year 1747, it was found that there was a duplicate Professorship of Humanity in St Salvator's College, which professorship, it is recorded with quaint brevity, was converted by the Act of Union into a Professorship of Civil History. This was the first step in the evolution of the Chair of Natural History as it now exists.

What the condition of the Chair of Civil History was during its occupancy—first by Professor Vilant and then by Professor Dick—no available record indicates, but Professor Forest, who held it for eight years subsequently, before his translation to the Chair of Natural Philosophy, was in the practice of teaching modern languages. Twenty years after its foundation another Professor, Hugh Cleghorn, who occupied the Chair from 1773 to 1793, had the greatest difficulty, to use his own words, in attempting 'to make a class'; and from one point of view the result of his labours was so unsatisfactory as to do little more than refund the value of the paper, pens, and ink with which he prepared his lectures. The professor, who was the grandfather of the late esteemed Dr Hugh Cleghorn of Stravithie, to whom, as will subsequently be shown, botany in St Andrews is largely indebted, seems, however, to have had some compensation, since he continued to hold the Chair though absent from Britain for a period of five years.[1] His successor, Dr Adamson (1793-1808), gave free lectures for three or four months every year, and his course in all probability consisted of a general outline of history.

The next occupant of the Chair (1808-1850) was Dr Ferrie, minister of the parish of Kilconquhar in Fife, who was appointed by the Earl of Cassilis, in whose family the patronage lay. He likewise made efforts to form a class of Civil History, 'accompanying' (in his course of lectures) 'the general outline

[1] In connection with the wars then waging on the continent of Europe.

of history with such reflections as would assist the student in forming rational views of the causes and consequences of events.' [1] He appears, however, probably, amongst other things, to the lack of attendance, to have lectured only one or two sessions out of his forty-two, though he regularly attended meetings of the college for discipline and business every Saturday, and was of great service in managing the complicated financial affairs of the college. So far, therefore, as regards teaching or original work, the professorship seems to have been chiefly nominal for this long period. The students of the day, it is true, were unable to take extra classes, that is, classes not in the regular curriculum for the Church, or for some of the liberal professions.[2] Moreover, their time was fully engaged by the compulsory classes, some of which occupied two or three hours daily.

There is little doubt that this condition of things gave anxiety to some of the able men who filled other chairs at this period, so that shortly before the Universities' Commission of 1827, the United College, with a prescience which did the members credit, took the important step of appointing a special lecturer on natural history, probably stimulated to this action by the vigorous influence of Dr Chalmers, then Professor of Moral Philosophy, who maintained, like the late eloquent Principal Cunningham of St Mary's College, that attendance at natural history, including botany, should be held indispensable to students of divinity, and the former of whom urged, with characteristic energy, the proper equipment of such a Chair. The first and only lecturer was Mr John M'Vicar, a licentiate of the Church (afterwards Dr M'Vicar of Moffat, and author of the *Philosophy of the Beautiful*), and whom in his later years (1857) the writer had the pleasure of hearing in Edinburgh as he discoursed in a fascinating manner on this subject with his ingenious models and diagrams. He lectured in the United College, first on the utility of the science,

[1] Evidence, *Univ. Com. Scot.*, 1827, p. 29. [2] *Op. cit.*

then on the inorganic and organic kingdoms. The inorganic kingdom he divided into three sections, according as the bodies are aerial, liquid, or solid, viz. the sciences of meteorology, hydrography, and mineralogy, afterwards proceeding with geology, 'which supports its theories upon the facts treated of in the three just named.' Half the session was thus occupied. The organised kingdom (zoology and botany) was then dealt with, botany appropriately fitting into the spring months, when Nature affords development of the plants—as Dr M'Vicar observes in his evidence before the Commissioners. In zoology the systematic arrangement of Cuvier was followed, commencing with man structurally and functionally, and passing down to the minutest animalculæ. This course was therefore very comprehensive, though the time for its delivery was limited. The lectures, which were free, were fairly supported, and amongst others Dr Chalmers regularly attended a course, taking deep interest in the subjects, and making copious notes like other students. John Goodsir (afterwards the distinguished Professor of Anatomy in Edinburgh) was also a student of Dr M'Vicar's during his last session in St Andrews. In addition to the interesting subject he dealt with, the charming personality of the lecturer could not but render his course attractive.

Dr M'Vicar further exerted himself to form the nucleus of a museum (which, however, had long before existed) in two halls over the common schools with their stone-benches for the students. These halls, formed by the division of one large hall by a wooden partition, were formerly used as dining-halls for secundars and ternars, and Dr M'Vicar describes them as of 'rather magnificent appearance, only they want light,' a feature (viz. the want of light) by no means surprising when it is remembered that the windows, which only occurred on the eastern side, that is, toward the college quadrangle, were carefully protected, for economic reasons, by strong wire-netting. Dr M'Vicar does not seem to have held the

lectureship for more than two sessions, and apparently no further effort was made to encourage natural science otherwise than by the cordial support at once given by the illustrious Sir David Brewster, on his appointment in 1838, in founding the Literary and Philosophical Society and the museum. Thus it was that the brothers John and Harry Goodsir and Edward Forbes joined with the distinguished physiologist John Reid, then Chandos Professor in St Andrews, in adding lustre, under Sir David Brewster, to the newly formed society.

The death of Dr Ferrie, the occupant of the Chair of Civil History, gave an opportunity for the introduction of a new feature in its history, viz. the presentation of a naturalist—Professor Macdonald (1850-1875), and the subject is now brought within the personal experience of the present writer. Hitherto, and for ninety-nine years, the Chair had been one of Civil History; henceforth it was to be a Chair of Natural History, though still entitled Civil and Natural History. What the views of Sir David Brewster originally were in regard to this appointment are unknown, but soon differences were manifest, the Principal retaining the lecture-room of natural history for his lectures on optics and allied subjects, whilst the Professor of Natural History had a small room on the ground floor.

The courses of lectures given by Professor Macdonald ranged over mineralogy and geology, physical geography, zoology, and botany. Complete courses on any of these, so far as can be made out, were never given. Thus, for example, in his seventh course (1856-57) the first eight lectures were devoted to mineralogy, including special remarks on precious stones; the next twenty-seven treated of zoology; while the last five were geological. In looking over the notes of these lectures, it is but just to say that one is struck by the large amount of information conveyed in an earnest and interesting manner in this brief course, which was attended, amongst others, by an army surgeon and an officer of H.M. Indian army.

Besides giving lectures in the small room, Professor Macdonald sometimes met his students in the museum, and examined special groups, such as minerals, geological or zoological specimens. He also met them at his house for disquisitions on his special theories of the skull, and other topics. Though no written examinations were held, several essays tested the earnestness of the students. Moreover, the Professor encouraged those interested in the subject by giving them free access to his collections at the end of the course, and some of the labels then affixed were found more than a quarter of a century afterwards. His valuable private collections of natural history specimens, indeed, were in themselves a source of real information to all who chose to examine them, and to the end of his life he constantly added to his stores.

On the whole, Professor Macdonald had no special leaning towards minute anatomical detail or to histology, and little to marine zoology ; but he had a gift for generalising and for launching theories of considerable ingenuity. He has left no original work of note behind him, but he deserves to be remembered, not only for his efforts under many difficulties, but for the large number of rare and valuable specimens in zoology, comparative anatomy, and mineralogy which he presented to the museum, and which have enabled his successors to illustrate their courses in a satisfactory manner.

The change from civil to natural history brought no addition to the students attending the class ; indeed, by and by great difficulty was experienced in having one at all, though the course was usually free. Nor was natural history at this period exceptional. The accomplished and genial Professor G. E. Day, an intimate friend of Edward Forbes and the Goodsirs, who then held the Chair of Medicine and Anatomy, encountered similar difficulties, and at best his classes were small, though of course they were not free.

Professor Macdonald, who held the Chair for a quarter of a century, was succeeded by Professor Alleyne Nicholson, who had taught in Edinburgh, Canada, and the Newcastle College of Science, and who lectured mainly on zoology, but also on palæontology and geology, in the former of which subjects he had done original work of note. As indicated, the class under Professor Macdonald had been free; now a small fee was instituted, and increased just before Professor Nicholson left, after seven years' service. The professor had no aid of any kind—skilled or unskilled—in performing his duties, and from a difficulty in regard to administration, the specimens in the museum were not at his disposal for teaching or other purposes.

On the transference of Professor Nicholson to Aberdeen, the present professor instituted a class of Practical Natural History in November 1882, and also had living marine things under observation, so as to form a small marine laboratory. The lectures were for the first time confined to zoology (including palæozoology), and this though it was understood that the Chair of Natural History in St Andrews included not only zoology and comparative anatomy, but botany, geology, palæontology, and mineralogy. Up to this period the class had very little apparatus, no lecture-drawings, only a single microscope, about a dozen microscopic slides, some jars containing unmounted specimens of common forms picked up on the beach after storms, and a few drawers of minerals and fossils. The addition of two thousand five hundred spirit-preparations illustrating the chief groups of animals, cabinets of named foreign shells, insects, osteological specimens, upwards of fifteen hundred coloured lecture-drawings (many from life), dissecting and other microscopes, a cabinet of microscopical preparations to illustrate the animal series, besides a miscellaneous collection of apparatus of various kinds, *e.g.* wood-blocks for issuing wood-cuts to the students, was therefore a considerable advance. Much of the microscopic

apparatus in both class and laboratory originated with an old and valued friend, Dr Fraser Thomson of Perth. Each lecture was now illustrated by a series of coloured drawings, a number of spirit and other preparations, occasionally by plates or original drawings as hand-specimens, and by a series of microscopic slides.

The foregoing observations in connection with the history of the Chair from its foundation—a period of one hundred and thirty-four years—show that the change from civil to natural history was more or less spontaneous. Moreover, the evolution of a single subject out of the half-dozen comprehended by the older Chair is a feature of interest. Popular favour and public utility, as well as the survival of the fittest, may have determined this condition of things; but whatever the cause may have been, it is a state pre-eminently suited in every way for St Andrews University, with its unique advantages for marine study and research. Every university may have chemistry, botany, and geology, but only one possesses within a stone-cast a bay teeming with marine life and situated between two large rivers—the Tay and the Forth, and with a littoral region unrivalled for its biological riches in sand, rocks, rock-pools, and mud.

In the University of Edinburgh, again, the change from a plurality of subjects, as embraced in the original Chair of Natural History, to one alone, took nearly one hundred years. The period of one hundred and thirty years in St Andrews, therefore, does not seem long, especially when it is remembered that natural history had no place in its Chair when founded in 1747, and that science has but slowly percolated where the older studies were dominant. That the occupant of a Chair should lecture on six different subjects so recently is a noteworthy fact, since each has now expanded into vast fields of research, and is burdened with a load of special literature in many languages.

It has been indicated that the foundation of a biological

station at St Andrews had been kept in view for many years. Accordingly, when it was found in 1882 and 1883 that the surplus funds of the Edinburgh Fisheries' Exhibition were to be devoted to such purposes, special efforts were made to obtain a moderate sum (£300) for this purpose. By the support of various societies in Edinburgh, however, the whole funds were placed at the disposal of Dr (now Sir) John Murray for the foundation of the Granton Laboratory, on which from first to last probably £7000 or £8000 have been spent. It is long since it was used for original research.

Efforts, nevertheless, were continued, and no opportunity was lost in pointing out the rare combination of circumstances which rendered St Andrews so peculiarly fitted for such a laboratory. This long-projected scheme was at last made practicable by a request that the Professor of Natural History should undertake the scientific work of the Trawling Commission in 1883. As the work was in progress in St Andrews Bay and elsewhere, it was clear that some kind of station was indispensable. The Chairman of the Commission (Lord Dalhousie) gave all the aid and encouragement in his power to meet this emergency. A grant from Parliament for the laboratory was obtained early in the year 1884, and administered through the Fishery Board for Scotland. Meanwhile the wooden hospital on the beach had been rented and occupied, so that many of the investigations for the Trawling Commission were at once carried out in it, with the aid of temporary apparatus formerly used for hatching salmon in Perthshire, as the laboratory was not fitted with pipes and tanks till the close of the year. This laboratory, independently of its special researches, greatly increased the facilities for study in connection with the class of natural history, and proved invaluable for enriching the museum.

The same year (1884) special exertions were made by the University to include a permanent biological laboratory, with its tanks and apparatus, within the grounds of the

United College.[1] Plans were drawn out by the Board of Works[2] showing how easily this and the extension of the museum could have been accomplished, but the proposal was not carried into execution.

In 1882 the Senate had nothing to offer as a practical room but the muniment-room with its stone floor and its stone roof, and this served as a practical class-room for two sessions; then, on the suggestion of Lord Dalhousie, the glass-top of a large table-case in the next room (originally intended as the retiring-room of the United College Hall, and long the sole class-room of Professor Macdonald) was removed, drawers for instruments fitted in, and both apartments were thus rendered available. No one disputed the Secretary for Scotland's authority. The same rooms were used for teaching practical botany two days a week on the institution of the lectures on botany in 1887. These rooms were ill-adapted for a practical class of any kind, both in regard to heating and lighting, yet they were better than those assigned by the University Court for zoology twenty years later. In the practical class (1882 to date) a regular course of instruction in the various types from Protozoa to mammals is carried out, specimens being supplied to students free. Each is taught microscopic manipulation and mounting, and encouraged to describe and to draw from nature, prizes being given for the best series of drawings, descriptions, and microscopical preparations. Remarkable forms are brought from the sea or the marine laboratory to the practical class or the lecture-room for examination and explanation. Students of St Andrews are freely permitted to work in the marine laboratory for study or research, and the same privilege is occasionally given to others. In the earlier years of the practical class, the demonstrator Dr Wilson, now lecturer on agriculture,

[1] *Vide* printed document 'Biological Laboratories and the Extension of the Museum,' St Andrews, 1884.

[2] Prepared by Mr Robertson, of H.M. Office of Works, Edinburgh.

and the members of the class gave occasional demonstrations of a popular kind on Friday afternoons.

In 1882 no other mode of storing the large collections in preparation-jars and bottles brought to St Andrews was available than the empty shelves (formerly fitted up for Professor Macdonald's books) in the gallery of the muniment-room. These had to be reached by a ladder, and conveyed up a long flight of stairs to the lecture-room. Next session, however, a series of temporary shelves were prepared in the open space under the lecture-room benches, and many of the jars and bottles were transferred to these. As year after year passed, however, the inconvenience attending the study of these by students became manifest, though they certainly were conveniently situated for lecture purposes. Accordingly, the Invertebrates were by and by placed in four large glass cases erected by the Government in the apartment at the roof of the museum containing the local collections, and both students and the public have now the opportunity of studying them with greater comfort and advantage.

Natural History in other Universities

Before making some general remarks on the Chair of Natural History in St Andrews, it may be useful to glance briefly at the Chairs of Natural History in other universities.

Thus, the Chair of Natural History in Edinburgh was founded in 1770, but the first Regius Professor, Dr Robert Ramsay, lectured only occasionally, and the museum of which he was the keeper, notwithstanding the efforts of Sir Andrew Balfour and Sir Robert Sibbald, contained few specimens. Dr Ramsay was succeeded in 1779 by Dr John Walker, who followed in his lectures the method then in vogue—discoursing on meteorology, hydrography, geology, mineralogy, botany, and zoology. He found it compatible with his duties in the University to carry on at the same time the ministry of Moffat,

and afterwards that of Colinton. Of a somewhat different type was Robert Jameson, the next occupant of the Chair. Before his appointment in 1804 he had learned a little medicine, had been a student of Walker's, and had specially studied mineralogy and geology under Werner at Freiberg. Though he was mainly an original inquirer in the two subjects just mentioned, and enriched the museum of the University greatly in these departments, yet he lost no opportunity of adding to the zoological collections. Thus many of the large quadrupeds were procured by his friends in India and Africa, while he was successful in securing the Dufresne collection of birds for the University. All this time, and, indeed, for fifty years, his lectures traversed nearly the same ground as his predecessors. His gifted successor, Edward Forbes, lectured only one summer, and thus had no time to develop the features of a new system, which undoubtedly would have been mainly zoological—the result of unique experience gathered in many seas and portrayed with the skill of an artist and a facile and persuasive eloquence all his own. Professor Allman, again, who followed Forbes in 1855, devoted the main part of his course to the study of zoology, a few concluding lectures only being allotted to physical geography, while the Thomsonian lectures on mineralogy were delivered in winter. For the first time the Chair became prominently one of zoology, and ever since it has almost exclusively dealt with that subject, for in 1871 the appointment of a Professor of Geology removed both this subject and mineralogy, as well as palæontology, from the Commission. Sir Wyville Thomson and Professor Ewart have lectured as zoologists only.[1]

Before leaving this important Chair, a brief remark may be made about the Edinburgh University museum. Though the

[1] For information concerning the various Chairs I am indebted to Professor Ewart, Professor Graham Kerr, Professor Arthur Thomson, the late Professor Allman, the late Professor Newton, the late Professor Alleyne Nicholson, and the late Professor Young.

old University collection—*e.g.* that between 1857 and 1860—was a classic one, and dear to the students of the period, the embodiment, in short, of Jameson's steady labours for half a century, dotted here and there by the evanescent hand of Forbes, and fostered by Allman under our eyes—yet it fell short, for the purpose of diffusing information, whether to the student or the public, of the fine zoological display in the Royal Scottish Museum. On this subject, therefore, while our sympathies go entirely with the Senatus and Sir Alexander Grant in the *Story of the University of Edinburgh*, our judgment bears testimony to the great advances which ample funds have enabled the Government Department to make in the zoological collection.

Formerly, in the University of Glasgow, lectures were given on geology and zoology, the latter specially for students of medicine and science. Arts' students—even those who took honours—were not required to attend, so that honours in science for the M.A. degree might have been obtained without attending a single science class. Now all is changed, the Department, since the appointment of Professor Graham Kerr, being a purely zoological one, with practical classes on the most modern system. For two years subsequently, it is true, the Chair included geology under its title of natural history, but the appointment of a Professor of Geology removed this subject entirely from the Commission. An extensive museum of natural history exists in connection with the Chair.

The University of Aberdeen, again, occupied a unique position in former years, for there every student, except those studying law, was compelled to attend the class of natural history. The course consisted of lectures on zoology in summer for medical students, with an optional practical class ; and in winter of a mixed course of ninety lectures on zoology, and geology for students of arts. A separate examination paper, moreover, was given in each department (viz. zoology and

geology) for the M.A. degree. Professor Alleyne Nicholson and others thought that the inclusion of natural history in the M.A. curriculum was not felt by the students of Aberdeen as a grievance. This Chair has likewise passed through various vicissitudes, for it once embraced botany and civil history, and, at a still earlier period, the professor also taught Latin and other subjects. Now the class is optional except for medical students, but large numbers (often a hundred) of arts' students still attend, and in their case the practical class is obligatory. Advanced and ordinary courses in zoology are given as well as a medical course. Besides, there is a lectureship on embryology, which in future will not be connected with any Chair. In addition, the following courses are mainly associated with the Chair of Natural History, viz. a Fishery Course of twelve meetings, a Parasitology Course of twelve meetings, and a Statistical Methods' Course of twelve meetings. The students of the advanced course of zoology must take at least one of the three last-named special courses. An excellent museum of natural history exists in connection with the Chair.

In the University of Oxford the modern Chair of Natural History sprang from the Linacre Professorship of Physiology, which was founded in 1854 at the expense of Merton College, but the first appointment was not made till 1860, when Professor Rolleston was elected, and at this time the new Museum was built. To this museum were transferred the old Ashmolean collections and those belonging to the Lees Reader of Anatomy of Christ Church. The professor was responsible for the teaching of human and comparative anatomy and physiology, and it is no wonder Rolleston pleaded for a division of the subjects. But though the University Commissioners in 1877 provided that the subjects should be restricted, this restriction did not take effect till Professor Rolleston's death in 1881. The Chair was now termed the Linacre Professorship of Human and Comparative

Anatomy, whilst Professor Burdon Sanderson was appointed Waynflete Professor of Physiology in 1883. Professor Rolleston was succeeded by Professor Moseley, and on his death Professor Ray Lankester held the Chair, which now dealt with comparative anatomy only. Professor Thomson, who had been Reader, was made Professor of Human Anatomy in 1893. Most of the undergraduates of the class are nominally arts' students and proceed to the B.A. degree. They begin with certain classical and literary examinations (responsions and an additional subject), and the natural science examinations are included in a comprehensive Faculty of Arts. The Professor of Comparative Anatomy (Zoology) is assisted by a lecturer in embryology and five demonstrators, two of whom are almost exclusively occupied with the foresters and the agriculturists. The bulk of the zoological collections are under the charge of the professor.

Oxford has in addition the Hope Professorship of Zoology, the holder of which has charge of the Entomological collections.

The natural history arrangements at the University of Cambridge, though of comparatively recent origin, are more complex. William Clark was Professor of Anatomy from 1817 to 1866, and such natural history as existed was taught by him, assisted by Dr Drosier of Caius, to which college he proved one of the greater benefactors at his death. The Professorship of Zoology and Comparative Anatomy was founded in 1866, Professor Alfred Newton being the first to occupy the Chair, and he had the assistance of a demonstrator. He was succeeded in 1907 by Professor Adam Sedgwick, and, on the transference of the latter to the Imperial College of Science, Professor Stanley Gardiner was appointed his successor in 1909. A Chair of Animal Morphology was created for Francis Maitland Balfour, the distinguished embryologist, in 1882, but on his death the same year it was discontinued. A university lecturer (Mr A. Sedgwick),

however, on the same subject was appointed, and the work of the laboratory was carried on by him and Walter Heape. In 1890 Mr Sedgwick was made Reader, a post equivalent to assistant professor. He was succeeded in 1907 by Mr Bateson, who a year later was made Professor of Biology, whilst Dr A. E. Shipley succeeded him as Reader. On Professor Bateson's transference to the Experimental Gardens, Mr R. C. Punnett, former assistant and lecturer in St Andrews, was appointed Professor of Biology in 1910. In 1874 Mr Osbet Salvin was made Strickland Curator of Birds, and he was succeeded by Dr Hans Gadow in 1883, and he discourses on the advanced morphology of vertebrates.

Cambridge has thus made remarkable advances in natural science during the last half century, and the vigour with which both teaching and research are carried out is well known. Much of this was due to the influence of Sir Michael Foster of Trinity College and to his pupil Francis Maitland Balfour. Moreover, the fund founded in his memory, viz. the Balfour Travelling Fellowship, has been of great service, and has contributed to the making of many able zoologists. Further, most of the colleges now have scholarships in natural science, such as Caius, King's, Christ's, St John's, Trinity, and Downing Colleges, and from time to time they have elected men to fellowships on account of their proficiency in zoology. The natural history museum of Cambridge is a valuable one, and contains many interesting forms in every zoological group. A special zoological keeper, who is not the Professor of Zoology, is appointed, an arrangement which is, perhaps, open to some objections.

The University Museum

Associated with the Chair of Natural History in each of the Scotch universities is a more or less extensive museum of natural history.

At St Andrews a general natural history collection seems to have existed for a very long time in the University. Thus what appears to be an armadillo was referred to in an old publication of the seventeenth century.[1] The collection, however, does not seem to have been extensive. When the lecturer on natural history (Dr M'Vicar) was appointed in 1827, he exerted himself to increase the collection; but it was not till the formation of the Literary and Philosophical Society in 1838 that steps were taken to secure proper accommodation for the specimens. One of the aims, indeed, of the society was to establish a museum in the University; and for this purpose a room was granted by the United College, and the first cases were made at the expense of the society. Under the vigorous leadership of Sir David Brewster, rapid progress was made during the next ten years, so that the new hall of the museum and adjoining apartments lately erected by the Government, and fitted with cases, were soon fairly filled by a general collection, consisting of minerals, geological, zoological, and botanical specimens. As mentioned, the influence of Sir David Brewster was of the utmost service in the early days of the museum, and amongst others, Dr Buist of India, Professor John Reid, Dr John Adamson, Dr Traill, Professor Macdonald, Dr Heddle, Robert Walker, and Dr Pettigrew deserve special notice during these and subsequent years. The Bruce collection of skeletons and preparations, the labour of a skilful local surgeon, was acquired by purchase at an early date, as also were various collections of fossils. A very fine series of Dura Den fossil fishes, the most valuable in the country, was added by the courtesy of the proprietor of the Den and the exertions of Dr Heddle, about 1860.

Between 1853 and 1857 the museum contained a miscellaneous collection, but was deficient in classification, though in regard to local crabs, shells, starfishes, and a few

[1] By Robert Johnston, *Scoto-Britanno*, Amsterdam, 1655.

other forms, the nomenclature and arrangement of the several authorities were adopted chiefly through the interest of Miss E. C. Otté. The mammals especially were very few. The management of the museum was in the hands of a joint committee of the Literary and Philosophical Society and the University, each paying half of the expenses of its maintenance, whilst the Government supplied the cases, on the understanding that the public were to have the privilege of access. The students, however, had no access to the museum, unless in charge of the professor, and the public paid a fee to the janitor who took visitors round. Previous to 1875, a noteworthy addition to the collection was made by Professor Macdonald, especially in specimens illustrating the comparative anatomy of vertebrates, and in a fine series of minerals and geological specimens. Principal Forbes likewise gave a large cabinet of minerals, gems, and fossils. The full advantage for teaching purposes, however, was not obtained till 1882. Since that date it has been largely utilised. At first students were only admitted by ticket with the sanction of the Senate and the Literary and Philosophical Society, but gradually free access was accorded to every student of the University.

In November 1882, comparatively few spirit-preparations existed in the museum, and these were for the most part of snakes. Active steps, however, were taken in 1883 to secure for the University a large series of spirit-preparations and dry specimens (stuffed and mounted) from the Fisheries' Exhibition in London. These chiefly consisted of fishes and invertebrates from India, Australia, South America, etc., though a large crocodile, a *Galeocerdo* (shark), and various piscatorial birds were included. Hundreds of valuable specimens were thus secured without cost, and the assistance of Dr Edward Pierson Ramsay, a relative of the late Mr Berry's law-agent in Australia, and Dr F. Day, who had charge of the Indian series, should be gratefully remembered. In 1884 the majority

of the spirit-preparations were mounted in jars, and the whole donation (with printed labels) was exhibited at a conversazione, presided over by Principal and Mrs Shairp, in the United College Hall in the spring of that year. In the same year the extensive type specimens, procured during the trawling expeditions connected with the Royal Commission under Lord Dalhousie, increased the value both of the museum and of the class collection. A series of stuffed and mounted birds and mammals and other forms was likewise procured from the Edinburgh Museum of Science and Art in exchange for various rare marine specimens. These and the type specimens of the eggs and young of the food-fishes, and examples from the *Challenger*, *Travailleur*, *Valorous*, *Porcupine*, and other exploring ships were exhibited at a second conversazione in the United College Hall early in 1885. Students, the public, and the fishing population had free access to both this and the previous conversazione.

Since 1882 a steady stream of British marine specimens has enriched the museum from various parts of the British coasts, and the local specimens (not a few new to Britain) have largely increased since the establishment of the marine laboratory in 1884. The series illustrating the eggs and life-history of the British food and other fishes may be referred to as of special interest and importance, and, so far as known, exceeds that of any other British collection. In one case alone there are between four hundred and five hundred jars, representing the eggs, larvæ, and various stages in the growth of the fishes.

Amongst other important collections received subsequently to the London Fisheries' Exhibition is a large series of young marsupials from the pouches, several examples of *Echidna*, and a young dugong from the Australian Museum through Dr Edward P. Ramsay. Many fresh specimens of monkeys, edentates, rodents, and other fresh forms from the Zoological Gardens, Regents Park, were forwarded by the kindness of

Mr F. E. Beddard. The late Professor D. J. Cunningham has also contributed largely in skeletons and spirit-preparations of the higher vertebrates, and in beautifully executed casts of the human brain *in situ*. Mr Alex. Thoms gave a large series of corals, shell-manufactures, and sponges; Mr Cyril Crossland an extensive collection of corals from the Red Sea; Professor Kishinonye, Japanese pear-shells, pearls, and coral; Dr Tosh, two fine examples of *Ceratodus* and a collection of pearl-shells and starfishes from Australia. Besides those formerly presented, three thousand one hundred and fifty spirit-preparations, including a cabinet illustrating the development of the salmon of the Tay from the egg, were handed over by the professor to the University. Lastly, by exchange of rare and unique marine forms with the Royal Scottish Museum, many well-mounted mammals and birds have been secured, the last consignment alone including more than fifty mounted mammals, ranging from a huge zebu ox to mice, a South American *Rhea*, and a large cassowary. Exchanges of a collection of the professors' rare forms also brought a valuable series from the Indian Museum through Dr Alcock and Dr Annandale, and from the Natural History Department of Edinburgh University.

With the exception of the foreign shells, the arrangement of the Museum during this period has been changed, the scattered representatives of the various groups having been drawn together, and a series of printed labels presented. But the present museum is quite overcrowded, and has for many years been in the main a storehouse for the preservation of the specimens, which are often superimposed.

Since 1882 a botanical collection has also been formed, many examples in spirit having been brought from Murthly, and largely increased by Dr Wilson, and since his period by Mr Robertson and other donors. Dr Cleghorn gave a general herbarium, Mr D. Smith a valuable cabinet of grasses, and Professor Bayley Balfour a large collection of textile

fibres and other specimens. Most of the botanical specimens are now in the botanical department at the Bute Medical Buildings. Further, a large series of geological, palæontological, and mineralogical specimens have been handed over for the equipment of the geological department.

Through the munificent gift of Mrs Bell Pettigrew, the University has now a spacious new museum with practical rooms for zoology and a curator's room at the Bute Medical Building, and she has also largely contributed to the furnishing of the museum with the most modern cases of iron. These have large plate-glass faces unbroken by bars, so that the maximum field is afforded for exhibition. To this fine museum the extensive and valuable and in some cases unique collections will be removed after the celebration of the five hundredth anniversary of the University. And thus the labour of many years and of nearly three generations will at last be adequately shown in a building which will ever be associated with the name of a valued colleague, whose skill in unravelling the fibres and nerves of the mammalian heart and other hollow organs, and whose pioneer researches on flight will also perpetuate his reputation.

An Interesting Comparison

A comparison of the state of science in the United College fifty-eight years ago with its condition to-day, and from personal experience, may be both interesting and instructive. In the early fifties of last century the University had as Chancellor the talented and versatile Duke of Argyll, who shone equally in the House of Lords and as President of the Geological Society of London, and whose scientific tastes and genial yet noble bearing made him a general favourite, while as Vice-Chancellor and Principal it had the distinguished discoverer in optics and cognate subjects, and the equally

brilliant writer, Sir David Brewster. Both shed remarkable dignity and lustre on the University, and received homage wherever science was known. The reputation of the Principal, and his fine presence, gave a tone to the college life of the period, and carried respect for the University throughout the country. Even the citizens of St Andrews were wont to point out to their young sons Sir David as he passed along the streets as one of the seven wisest men in the world. In him the students of the day were brought face to face with a high type of intellectual force, of unflagging industry, and well-directed aims. With signal devotion to the subjects he had taken in hand, he every year produced important results in the form of original papers—no less than about one hundred and eighteen scientific communications marking his twenty years' tenure of the Principalship of this University. While thus busy in extending the boundaries of science, he was ever mindful of his duties to the University. Besides popular lectures in the city, he gave various courses of lectures on optics and cognate subjects in the present natural history class-room. His dignified yet kindly bearing, his clear and elegant diction, together with his great reputation, made such courses unusually successful, and the students of the day were ever eager to listen to him. Besides, his whole life shone as an example and a stimulus to every thoughtful student within the University.

Sir David, moreover, may be said to have originated the Literary and Philosophical Society of St Andrews in connection with the University. He was its President, and so long as he remained in the city, the work of the society was carried on with vigour and regularity. His influence and inspiration attracted men like the brothers John and Harry Goodsir, Edward Forbes, John Reid, David Page, and many others, whilst the leading citizens, from Sir Hugh Lyon Playfair, then Provost, downwards, cordially joined in the proceedings. As will be observed in the remarks on the

museum, one of the main objects of the society was to found a museum in connection with the University, and Sir David lost no opportunity of using his influence at home and abroad to carry out this purpose.

Under this distinguished Principal the Science Chairs in the University were—Mathematics, Natural Philosophy, Civil History (including Natural History), Medicine and Anatomy, and Chemistry.

The Chair of Mathematics was occupied by Professor Thomas Duncan, a native of Fife, the friend of Dr Chalmers, and the author of a text-book entitled *Elements of Plane Geometry.* Professor Duncan was an enthusiastic and capable teacher, but at this period advanced age and ill-health compelled him in 1854 to find an assistant professor in Dr Lees of the School of Arts in Edinburgh, who had many difficulties to encounter in the teaching of the three mathematical classes.

Professor Fischer, an able graduate of Cambridge, held the Chair of Natural Philosophy. His abilities were great, though he only published a small work on logarithms, and one paper on a 'Problem in Plane Optics' in the *Cambridge Mathematical Journal,* and his prelections were eagerly followed by the hard-working students. Though a German by birth, he spoke English with considerable fluency. His strong point was mathematics, and some years after the period mentioned (1853-57) he was transferred to the Chair of Mathematics in the University. No practical class in connection with natural philosophy was then in existence, but Professor Fischer demonstrated privately to earnest students the working of many interesting philosophical instruments and showed various microscopic preparations.

The occupant of the Chair of Civil History (really Natural History) was Professor Macdonald. At the period mentioned the lectures were more or less intermittent and attended by few students, and occasionally some of these were amateurs. The lectures embraced mineralogy, geology, and palæontology,

as well as botany and zoology, the latter subject, however, receiving a large amount of attention. By the events already alluded to, the professor was shut out of the natural history class-room, and gave his lectures in the retiring-room of the College Hall, where the class of practical zoology, after 1882, met for twenty years. No large cases were then present, so that the very fine mineralogical and zoological specimens belonging to Dr Macdonald, and which he subsequently presented to the museum, had ample accommodation. Systematic study of any one branch of the subjects mentioned, however, was difficult, and though essays in the case of zoology were prescribed, it was rare to find a writer. The value of close contact with the fine collections of the professor, and his skill in the comparative anatomy of the vertebrates, made the course of real practical utility to those interested. Professor Macdonald was the author of eight or ten papers, chiefly on vertebrate homologies.

A cultured physician, Professor George E. Day, held the Chair of Medicine and Anatomy. He gave two courses of lectures, one on physiology and another on comparative anatomy. As the fellow-student of John Goodsir, Edward Forbes, and John Reid, his opportunities, both in regard to physiology and comparative anatomy, had been great. His own labours, however, had been chiefly in the field of physiological chemistry, and he likewise translated Lehman's work on this subject. His lectures on physiology and comparative anatomy were both gracefully delivered from manuscript and full of information, and occasionally some of the living forms from the beach, such as *Cydippe*, were brought to the class-room, through the interest of the enthusiastic and talented Miss E. C. Otté. No practical class was held, though microscopical demonstrations occasionally took place in the professor's house. The influence and encouragement emanating both from Professor Day and Miss Otté must have been felt by many a student of the period, and by none more

than the writer. Besides his translation of Lehman's Chemistry, Dr Day published reports on the progress of Animal Chemistry, and a work on the Diseases of Old Age.

The first Professor of Chemistry then taught in the University, the Chair having been founded only in 1840. Professor Connell's health, however, gave way in 1856, and an assistant (Dr Heddle) lectured during the session 1856-57. Professor Connell's lectures were given with great care and lucidity, and then, as now, the class was a popular one with the students of arts, science, and medicine, as well as with the general public. Dr. Connell, indeed, gave for a year or two special courses on agricultural chemistry on the afternoons of Monday, to which farmers and the public were admitted free, though they had occasionally to run the gauntlet of volleys of snowballs from the younger students of the University. Dr Heddle's first course consisted of both inorganic and organic chemistry, with remarks on the analysis of minerals at intervals. There was no practical class, and the student at this time had to depend on private resources for chemical experiments, and many adventures were associated with these home-laboratories. Professor Connell made important discoveries in regard to the dew-point, the analyses of many minerals (including brewsterite), iodic acid, naphthalene, action of voltaic electricity on alcohol, action of waters on lead, and the chemistry of fossil scales, no less than forty papers of note being attached to his name. Professor Connell was a chemist of great originality, and, working under many difficulties, his researches were an honour to him and to his University.

A consideration of the foregoing remarks shows that at this time (1853-1857) the Principal of the University towered far above the occupants of the Chairs in original investigation, unceasing industry, and in European reputation. Though between seventy-three and seventy-seven years of age, the venerable philosopher had all the ardour of youth in his studies, and stood forth as a splendid example to every

student of his day, and not only to these, but to every student in all time. When this distinguished man of science, then Principal of the University of Edinburgh, passed to his rest in 1868, he left a record of at least eight separate works, and no less than three hundred and thirty-six scientific papers in his own name, and five joint communications, the result of marvellous ability and stupendous labour. Besides these, his daughter (who inherited much of her father's talent) gives a list of seventy-five reviews and articles Sir David wrote for the *North British Review*—on subjects ranging from Lord Rosse's Reflecting Telescope to De Quatrefages' Rambles of a Naturalist.

While the science-student of the period thus had a splendid example at the head of affairs, and science had made certain advances in regard to the curriculum, still much remained to be done. In contrast with the opportunities then available in the University of Edinburgh, the follower of science in these years must have felt out of touch with his surroundings, and he only breathed freely and braced himself for real effort amidst the free atmosphere, the encouragement, the broad views and wide sympathies of the larger University. At least the great prominence of the subjects considered necessary in training for divinity, and the absence of systematic stimulation in science, must, in some degree, have had this tendency. Even the distinguished presidency of the illustrious Sir David Brewster, and subsequently the self-denying example of Principal Forbes, were not sufficient to counteract the tendency which, from the foundation of the University, had made the purely classical and literary subjects paramount. The science student had no practical classes in chemistry, physiology, natural history, or natural philosophy. There were no lectures on botany and no botanic garden. Moreover, the museum was antiquated in arrangement, and by no means easily accessible.

And now, after the lapse of fifty-four years, what is the condition of science in the University ? The old Chancellor

has been succeeded by Lord Balfour of Burleigh, the Rector is one of the most eloquent nobles in the land, whilst the Vice-Chancellor, Sir James Donaldson, is distinguished in classics. Yet though the present heads of the University are not specialists in scientific subjects, the progress made in the teaching of science since 1857, and especially since 1882, has been remarkable, as the following brief notes will indicate.

To-day the teaching of mathematics has been greatly extended by additional honours classes, tutorial classes, and by the appointment of a lecturer on applied mathematics. The great emphasis now laid on a proper grasp of principles rather than a mere facility in applying rules has enabled the student to carry his studies considerably further than formerly, and a very superficial comparison of the present-day degree papers with those of half a century ago will show how real the advance has been. Much of this progress is probably due to the better knowledge of the subject with which the student enters the University.

In addition to the ordinary lectures on natural philosophy, the student now has an opportunity of attending classes of practical physics, both senior and junior, under a demonstrator, and of performing with his own hands the experiments formerly seen from a distance, and of becoming acquainted with the various instruments used in the manipulations. A new class-room, a spacious and well-appointed museum for apparatus, and a large detached building of one story, equipped with the necessary apparatus for practical physics, have been added to the department.

The changes in connection with the Chair of Natural History, as indicated on pp. 274-280, are more numerous. It is no longer a Chair including a wide range of subjects under its title, for it is now one of Zoology. Instead of the single short course of the old system, there are at least four courses, each with its practical class. In 1882 it had little or no apparatus and no drawings. Now it has between two

and three thousand coloured lecture drawings, thousands of microscopic preparations, and every kind of apparatus necessary for the thorough knowledge of the subject. Its spirit-preparations and skeletons form an extensive and bulky series, not to allude to the type-series connected with the scientific investigations on trawling and on the salmon. Up to this moment, however, the accommodation has remained the same as in 1882. Attached to the new Pettigrew Museum, however, a new and more spacious practical class-room has been formed, but no lecture-room has been provided.

While as yet there has been no expansion of the class-room accommodation for the natural history department, the institution by the Government of a marine laboratory in 1884 has led to further developments in marine work, for in 1896 the Gatty Marine Laboratory was opened under the auspices of the University, the munificent gift of Dr Charles Henry Gatty of Felbridge Place, Sussex. This affords the students, and still more the graduates, facilities for marine researches—both zoological and botanical—unknown under the old regime. The list of works and researches connected with the department will be found in the brochure on the Marine Laboratory.

In the class of physiology many advances have likewise occurred. Instead of the two short courses of physiology and comparative anatomy, a complete course of physiology, with practical work of the most modern type, is now the rule, and the apparatus has been largely increased. Moreover, a complete suite of practical rooms has been provided in the Bute Medical Buildings with adjoining lecture-room. Thus the views of the late Universities Commission, that the Chandos Chair should cease, have not been carried out, and the Chair of John Reid, George Edward Day, and James Bell Pettigrew is now more firmly rooted in St Andrews than ever.

In the course of half a century great improvements have been made in the department of chemistry, and the whole

treatment of the subject has been revolutionised to keep pace with the development of the subject and with the increasing demands of practical work and original research. Fifty years ago, only a single theoretical course, which included both inorganic and organic chemistry, was given. At present there are three distinct lecture courses (general, special, and honours) with corresponding practical classes. The spacious practical laboratory, the generous gift of the late Mr Purdie of Castlecliffe, now affords the student of chemistry in St Andrews facilities which are not excelled in other and larger universities.

A more notable development is the progress made in post-graduate instruction. The successful efforts made by Professor Purdie to induce his best students to undertake research work, culminated recently in the institution of a special research department in chemistry. A new laboratory, specially designed and reserved for research, was presented to the University by Professor Purdie, and opened in 1905. The department is equipped with every facility for original work, and possesses an extensive library of research literature. The cost of special apparatus and chemicals is met out of an endowment fund, so that post-graduate workers are thus able to carry out their investigations without expense. Under these favourable conditions, which are almost unique in this country, a steady succession of the best students of chemistry have, in recent years, taken advantage of the facilities afforded by the laboratory, and taken an active share in the research work of the department.

While the classes in existence half a century ago have therefore made great advances in every respect, this does not complete the survey. Since 1887 the lectureship in botany—with senior and junior courses—has come into existence as an offshoot from the natural history class. The first course was given in the winter of 1887 by Dr John H. Wilson, the demonstrator of zoology, and this before any teaching on the subject was instituted in Dundee. Very shortly after-

wards a botanic garden was laid out by Dr Wilson and Mr Berwick in an old garden rented from St. Mary's College, and made available for the students. A few years later Dr Cleghorn of Stravithie, who took a keen interest in this development, and who had been at the opening of the garden in the summer of 1888, privately intimated to the Professor of Natural History that he wished to give £1000 to his Chair. Botany, however, was struggling under difficulties, and it was suggested that as Dr Cleghorn was himself a well-known botanist, and, besides, had lectured on forestry in the University, it would be a graceful act to assign it to the lectureship in botany, or to a Chair in St Andrews if that should ultimately be founded. This was done anonymously in accordance with Dr Cleghorn's wish, and not even the Principal of the University had any clue to identification till the death of the generous donor. Dr Cleghorn also presented various botanical lecture-drawings, a herbarium, and numerous other specimens. The lectureship was thus made secure, and a boon conferred on the University by the institution of a new subject at once popular and important in science, medicine, and arts. For some years the lectureship continued in connection with the demonstratorship in zoology, until in 1893 the additional funds accruing to the University by the new Act enabled the Court to institute an independent lectureship, to which Mr A. R. Robertson, who had held both posts (zoological and botanical) for some time, was appointed. Botany has now spacious accommodation in the Bute Medical Buildings, a botanic garden is attached and also a series of glass-houses, experimental rooms, and other conveniences, the erection of the conservatories having been generously defrayed by Mrs Pettigrew. The courses in botany consist of general, special, and honours classes, practical classes being attached to each section, and opportunities are given to advanced students for original research.

In former years, though no lectures were given in the

University, botany was not neglected in St Andrews. The late Mr Charles Howie was an excellent field botanist, and few had a better knowledge of the mosses, his work on this subject, illustrated by the actual specimens on each page, being even now highly esteemed. He also published a work on the remarkable trees of Fife. Mr. Howie gave a herbarium to the botanical department, and his collection of algæ to the Gatty Marine Laboratory, where also the extensive and very fine collection of British and foreign algæ made by the late Mrs Alfred Gatty now is, along with her library on the subject.

In 1900 a lectureship in Agriculture was instituted, and Dr J. H. Wilson appointed to the post. Well known for his experiments on hybridisation, and for his botanical researches, such a lectureship is in able hands. His extensive knowledge of American agricultural schools, and his more recent experiences as scientific adviser to the Agricultural Commission in Australia, give him a wide grasp of the subject.

In 1905 a lectureship in geology was also created, and Dr Jehu appointed to the office, but he has at present to lecture alternate sessions in St Andrews and Dundee, so that the scope of the subject in each place is thus more or less interfered with. The department has spacious rooms in the Bute Medical Buildings, and is well equipped with large collections of specimens, apparatus, and lecture-drawings.

Other changes have still to be recorded. The splendid donation of the Berry Trust awakened fresh interest in the development of the two *anni medici* so long and so resolutely advocated for St Andrews. It was felt that it would be a great gain both to the student and to the public if, instead of the *one year*, which for at least a century has been obtainable at St. Andrews, *two years'* medical study, under such healthy and yet truly academic auspices, could be instituted. The two years' course of medical study is now an accomplished fact, a benefit largely due to the loyal support of the medical graduates of the University, headed by Sir Benjamin

Ward Richardson, and by the unswerving aid of the Rector, Lord Bute, who in the most generous spirit at once provided the spacious medical buildings for anatomy, physiology, botany, and materia medica with their practical and experimental rooms and museums, and still further added to his already munificent gifts by endowing the Chair of Anatomy. The gain is not alone to medicine : science is no less benefited, for anatomy and physiology, like zoology and botany, may with advantage be studied by students of other Faculties.

Again, while no reward other than a class prize fell to the lot of a science or medical student half a century ago, special and valuable prizes now exist in chemistry and zoology, and additional prizes in the class of mathematics. Further, in 1890 the 1851 Exhibition Science Research Scholarships were made available for this and other British universities, and since that period the University has been represented by numerous excellent original workers. The Berry Scholarships have also been instituted, and are held by distinguished graduates who carry on original researches subsequent to graduation. The science students of the University also share in the benefits of the post-graduate scheme of the Carnegie Trust, and, in recent years, a creditable number of Research Fellowships and Scholarships have been gained by St Andrews' students.

The last two or three decades thus mark an era in the life of the University—an era characterised by ceaseless endeavours to place science, so long 'fed on the crumbs which fell from the arts' table,'[1] on a proper footing—both in the curriculum and in general culture. The substantial progress made during the period embraced by the foregoing recollections must afford profound gratification to all who desire to see scientific study attain an honourable position in the intellectual life of the University.

[1] The remark of a Classical Professor in former days.

WILLIAM CARMICHAEL M'INTOSH

MAGNALIA NATURÆ: OR THE GREATER PROBLEMS OF BIOLOGY

Being the Presidential Address delivered to the Zoological Section of the British Association August 31st 1911

The science of zoology, all the more the incorporate science of biology, is no simple affair, and from its earliest beginnings it has been a great and complex and many-sided thing. We can scarce get a broader view of it than from Aristotle, for no man has ever looked upon our science with a more far-seeing and comprehending eye. Aristotle was all things that we mean by 'naturalist' or 'biologist.' He was a student of the ways and doings of beast and bird and creeping thing; he was morphologist and embryologist; he had the keenest insight into physiological problems, though his age lacked that knowledge of the physical sciences without which physiology can go but a little way: he was the first and is the greatest of psychologists; and in the light of his genius biology merged in a great philosophy.

I do not for a moment suppose that the vast multitude of facts which Aristotle records were all, or even mostly, the fruit of his own immediate and independent observation. Before him were the Hippocratic and other schools of physicians and anatomists. Before him there were nameless and forgotten Fabres, Rœsels, Réaumurs, and Hubers, who observed the habits, the diet, and the habitations of the sand-wasp or the mason-bee; who traced out the little lives, and discerned the vocal organs, of grasshopper and cicada;

and who, together with generations of bee-keeping peasants, gathered up the lore and wisdom of the bee. There were fishermen skilled in all the cunning of their craft, who discussed the wanderings of tunny and mackerel, swordfish or anchovy; who argued over the ages, the breeding places and the food of this fish or that; who knew how the smooth dogfish breeds, two thousand years before Johannes Müller; who saw how the male pipefish carries its young, before Cavolini; and who had found the nest of the nest-building rock-fishes, before Gerbe rediscovered it almost in our own day. There were curious students of the cuttle-fish (I sometimes imagine they may have been priests of that sea-born goddess to whom the creatures were sacred), who had diagnosed the species, recorded the habits, and dissected the anatomy of the group, even to the discovery of that strange hectocotylus arm that baffled Della Chiaje, Cuvier and Koelliker, and that Verany and Heinrich Müller re-explained.

All this varied learning Aristotle gathered up and wove into his great web. But every here and there, in words that are unmistakably the master's own, we hear him speak of what are still the great problems and even the hidden mysteries of our science; of such things as the nature of variation, of the struggle for existence, of specific and generic differentiation of form, of the origin of the tissues, the problems of heredity, the mystery of sex, of the phenomena of reproduction and growth, the characteristics of habit, instinct, and intelligence, and of the very meaning of Life itself. Amid all the maze of concrete facts that century after century keeps adding to our store, these, and such as these, remain the great mysteries of natural science—the *magnalia naturæ*, to borrow a great word from Bacon, who in his turn had borrowed it from St Paul.

Not that these are the only great problems for the biologist, nor that there is but a single class of great problems in biology. For Bacon himself speaks of the *magnalia naturæ, quoad*

usus humanos; the study of which has for its objects 'the prolongation of life or the retardation of age, the curing of diseases counted incurable, the mitigation of pain, the making of new species and transplanting of one species into another,' and so on through many more. Assuredly, I have no need to remind you that a great feature of this generation of ours has been the way in which Biology has been justified of her children, in the work of those who have studied the *magnalia naturæ, quoad usus humanos.*

But so far are biologists from being nowadays engrossed in practical questions, in applied and technical zoology, to the neglect of its more recondite problems, that there never was a time when men thought more deeply or laboured with greater zeal over the fundamental phenomena of living things; never a time when they reflected in a broader spirit over such questions as purposive adaptation, the harmonious working of the fabric of the body in relation to environment, and the interplay of all the creatures that people the earth; over the problems of heredity and variation; over the mysteries of sex, and the phenomena of generation and reproduction, by which phenomena, as the wise woman told, or reminded, Socrates, and as Harvey said again (and for that matter, as Coleridge said, and Weismann, but not quite so well),—by which, as the wise old woman said, we gain our glimpse of insight into eternity and immortality. These, then, together with the problem of the Origin of Species, are indeed *magnalia naturæ*; and I take it that inquiry into these, deep and wide research specially directed to the solution of these, is characteristic of the spirit of our time, and is the password of the younger generation of biologists.

Interwoven with this high aim which is manifested in the biological work of recent years, is another tendency. It is the desire to bring to bear upon our science, in greater measure than before, the methods and results of the other sciences,

both those that in the hierarchy of knowledge are set above and below, and those that rank alongside of our own.

Before the great problems of which I have spoken, the cleft between zoology and botany fades away, for the same problems are common to the twin sciences. When the zoologist becomes a student not of the dead but of the living, of the vital processes of the cell rather than of the dry bones of the body, he becomes once more a physiologist, and the gulf between these two disciplines disappears. When he becomes a physiologist, he becomes *ipso facto* a student of chemistry and of physics. Even mathematics has been pressed into the service of the biologist, and the calculus of probabilities is not the only branch of mathematics to which he may usefully appeal.

The physiologist has long had as his distinguishing characteristic, giving his craft a rank superior to the sister branch of morphology, the fact that in his great field of work, and in all the routine of his experimental research, the methods of the physicist and the chemist, the lessons of the anatomist, and the experience of the physician, are inextricably blended in one common central field of investigation and thought. But it is much more recently that the morphologist and embryologist have made use of the method of experiment, and of the aid of the physical and chemical sciences,—even of the teachings of philosophy: all in order to probe into properties of the living organism that men were wont to take for granted, or to regard as beyond their reach, under a narrower interpretation of the business of the biologist. Driesch and Loeb and Roux are three among many men, who have become eminent in this way in recent years, and their work we may take as typical of methods and aims such as those of which I speak. Driesch, both by careful experiment and by philosophic insight, Loeb by his conception of the dynamics of the cell and by his marvellous demonstrations of chemical and mechanical fertilisation, Roux with

his theory of auto-determination, and by the labours of the school of *Entwickelungsmechanik* which he has founded, have all in various ways, and from more or less different points of view, helped to reconstruct and readjust our ideas of the relations of embryological processes, and hence of the phenomenon of Life itself, on the one hand to physical causes (whether external to or latent in the mechanism of the cell), or on the other to the ancient conception of a Vital Element, alien to the province of the physicist.

No small number of theories or hypotheses, that seemed for a time to have been established on ground as firm as that on which we tread, have been reopened in our day. The adequacy of natural selection to explain the whole of organic evolution has been assailed on many sides; the old fundamental subject of embryological debate between the evolutionists or preformationists (of the school of Malpighi, Haller, and Bonnet), and the advocates of epigenesis (the followers of Aristotle, of Harvey, of Caspar Fr. Wolff, and of Von Baer), is now discussed again, in altered language, but as a pressing question of the hour; the very foundations of the cell-theory have been scrutinised, to decide (for instance) whether the segmented ovum, or even the complete organism, be a colony of quasi-independent cells, or a living unit in which cell-differentiation is little more than a superficial phenomenon; the whole meaning, bearing, and philosophy of evolution has been discussed by Bergson, on a plane to which neither Darwin nor Spencer ever attained; and the hypothesis of a Vital Principle, or vital element, that had lain in the background for near a hundred years, has come into men's mouths as a very real and urgent question, the greatest question for the biologist of all.

In all ages the mystery of organic form, the mystery of growth and reproduction, the mystery of thought and consciousness, the whole mystery of the complex phenomena

of life, have seemed to the vast majority of men to call for description and explanation in terms alien to the language which we apply to inanimate things: though at all times there have been a few who sought, with the materialism of Democritus, Lucretius or Giordano Bruno, to attribute most, or even all, of these phenomena to the category of physical causation.

For the first scientific exposition of Vitalism, we must go back to Aristotle, and to his doctrine of the three parts of the tripartite soul: according to which doctrine, in Milton's language, created things 'by gradual change sublimed, To vital spirits aspire, to animal, To intellectual!' The first and lowest of these three, the ψυχὴ ἡ θρεπτική, by whose agency nutrition is effected, is ἡ πρώτη ψυχή, the inseparable concomitant of life itself. It is inherent in the plant as well as in the animal, and in the Linnaean aphorism, *vegetabilia crescunt et vivunt*, its existence is admitted in a word. Under other aspects, it is all but identical with the ψυχὴ αὐξητική and γεννητική, the soul of growth and of reproduction: and in this composite sense it is no other than Driesch's 'Entelechy,' the hypothetic natural agency that presides over the form and formation of the body. Just as Driesch's psychoid or psychoids, which are the basis of instinctive phenomena, of sensation, instinct, thought, reason, and all that directs that body which entelechy has formed, are no other than the αἰσθητική, whereby *animalia vivunt et sentiunt*, and the διανοητική, to which Aristotle ascribes the reasoning faculty of man. Save only that Driesch, like Darwin, would deny the restriction of νοῦς, or reasoning, to man alone, and would extend it to animals, it is clear, and Driesch himself admits,[1] that he accepts both the vitalism and the analysis of vitalism laid down by Aristotle.

The πνεῦμα of Galen, the *vis plastica*, the *vis vitæ forma-*

[1] *Science and Philosophy of the Organism* (Gifford Lectures), ii. p. 83, 1908.

trix, of the older physiologists, the *Bildungstrieb* of Blumenbach, the *Lebenskraft* of Paracelsus, Stahl and Treviranus, 'shaping the physical forces of the body to its own ends,' 'dreaming dimly in the grain of the promise of the full corn in the ear'[1] (to borrow the rendering of an Oxford scholar), these and many more, like Driesch's 'Entelechy' of to-day, are all conceptions under which successive generations strive to depict the something that separates the earthy from the living, the living from the dead. And John Hunter described his conception of it in words not very different from Driesch's, when he said that his principle, or agent, was independent of organisation, which yet it animates, sustains, and repairs; it was the same as Johannes Müller's conception of an innate 'unconscious idea.'

Even in the Middle Ages, long before Descartes, we can trace, if we interpret the language and the spirit of the time, an antithesis that, if not identical, is at least parallel to our alternative between vitalistic and mechanical hypotheses. For instance, Father Harper tells us that Suarez maintained that in generation and development a Divine Interference is postulated, by reason of the perfection of living beings; in opposition to St Thomas, who (while invariably making an exception in the case of the human soul) urged that, since the existence of bodily and natural forms consists solely in their union with matter, the ordinary agencies which operate on matter sufficiently account for them.[2]

[1] *Cit.* Jenkinson (*Art.* 'Vitalism' in *Hibbert Journal*, April 1911), who has given me the following quotation: 'Das Weitzenkorn hat allerdings Bewusstsein dessen was in ihm ist und aus ihm werden kann, und traümt wirklich davon. Sein Bewusstsein und seine Traüme mögen dunkel genug sein'; Treviranus, *Erscheinungen und Gesetze des organischen Lebens*, 1831.

[2] 'Cum formarum naturalium et corporalium esse non consistat nisi in unione ad materiam, ejusdam agentis esse videtur eas producere, cujus est materiam transmutare. Secundo, quia cum hujusmodi formæ non excedant virtutem et ordinem et facultatem principiorum agentium in natura, nulla videtur necessitas eorum originem in principia reducere altiora.' Aquinas, *De Pot. Q.*, iii. a 11. Cf. Harper, *Metaphysics of the School*, iii. 1, p. 152.

But in the history of modern science, or of modern physiology, it is of course to Descartes, that we trace the origin of our mechanical hypotheses,—to Descartes, who, imitating Archimedes, said 'Give me matter and motion, and I will construct the universe.' In fact, leaving the more shadowy past alone, we may say that it is since Descartes watched the fountains in the garden, and saw the likeness between their machinery of pumps and pipes and reservoirs to the organs of the circulation of the blood, and since Vaucanson's marvellous automata lent plausibility to the idea of a 'living automaton,' it is since then that men's minds have been perpetually swayed by one or other of the two conflicting tendencies, either to seek an explanation of the phenomena of living things in physical and mechanical considerations, or to attribute them to unknown and mysterious causes, alien to physics, and peculiarly concomitant with Life. And some men's temperaments, training, and even avocations, render them more prone to the one side of this unending controversy, as the minds of other men are naturally more open to the other. As Kühne said a few years ago at Cambridge, the physiologists have been found for several generations leaning on the whole to the mechanical or physico-chemical hypothesis, while the zoologists have been very generally on the side of the Vitalists.

The very fact that the physiologists were trained in the school of physics, and the fact that the zoologists and botanists relied for so many years upon the vague undefined force of 'heredity' as sufficiently accounting for the development of the organism, an intrinsic force whose results could be studied but whose nature seemed remote from possible analysis or explanation, these facts alone go far to illustrate and to justify what Kühne said.

Claude Bernard held that mechanical, physical and chemical forces summed up all with which the physiologist has to deal. Verworn defined physiology as 'the chemistry

of the proteids ' ; and I think that another physiologist (but I forget who) has declared that the mystery of Life lay hidden in ' the chemistry of the enzymes.' But of late, as Dr Haldane showed in an address a couple of years ago, it is among the physiologists themselves, together with the embryologists, that we find the strongest indications of a desire to pass beyond the horizon of Descartes, and to avow that physical and chemical methods, the methods of Helmholtz, Ludwig, and Claude Bernard, fall short of solving the secrets of physiology. On the other hand, in zoology, resort to the method of experiment, the discovery, for instance, of the wonderful effects of chemical or even mechanical stimulation in starting the development of the egg, and again the ceaseless search into the minute structure, or so-called mechanism, of the cell, these I think have rather tended to sway a certain number of zoologists in the direction of the mechanical hypothesis.

But on the whole, I think it is very manifest that there is abroad on all sides a greater spirit of hesitation and caution than of old, and that the lessons of the philosopher have had their influence on our minds. We realise that the problem of development is far harder than we had begun to let ourselves suppose: that the problems of organogeny and phylogeny (as well as those of physiology) are not comparatively simple and well-nigh solved, but are of the most formidable complexity. And we would, most of us, confess, with the learned author of *The Cell in Development and Inheritance*, that we are utterly ignorant of the manner in which the substance of the germ-cell can so respond to the influence of the environment as to call forth an adaptive variation ; and again, that the gulf between the lowest forms of life and the inorganic world is as wide, if not wider, than it seemed a couple of generations ago.[1]

While we keep an open mind on this question of Vitalism,

[1] Wilson, *op. cit.*, 1906, p. 434.

or while we lean, as so many of us now do, or even cling with a great yearning, to the belief that something other than the physical forces animates and sustains the dust of which we are made, it is rather the business of the philosopher than of the biologist, or of the biologist only when he has served his humble and severe apprenticeship to philosophy, to deal with the ultimate problem. It is the plain bounden duty of the biologist to pursue his course, unprejudiced by vitalistic hypotheses, along the road of observation and experiment, according to the accepted discipline of the natural and physical sciences; indeed I might perhaps better say the physical sciences alone, for it is already a breach of their discipline to invoke, until we feel we absolutely must, that shadowy force of 'heredity,' to which, as I have already said, biologists have been accustomed to ascribe so much. In other words, it is an elementary scientific duty, it is a rule that Kant himself laid down,[1] that we should explain, just as far as we possibly can, all that is capable of such explanation, in the light of the properties of matter and of the forms of energy with which we are already acquainted.

It is of the essence of physiological science to investigate the manifestations of Energy in the body, and to refer them, for instance, to the domains of heat, electricity or chemical activity. By this means a vast number of phenomena, of chemical and other actions of the body, have been relegated to the domain of physical science, and withdrawn from the mystery that still attends on life: and by this means, continued for generations, the physiologists, or certain of them, now tell us that we begin again to descry the limitations of physical inquiry, and the region where a very different hypothesis insists on thrusting itself in. But the morphologist has not gone nearly so far as the physiologist in the use of physical methods. He sees so great a gulf between the crystal and the cell, that the very fact of the physicist

[1] In his *Critique of Teleological Judgment.*

and the mathematician being able to explain the form of the one, by simple laws of spatial arrangement where molecule fits into molecule, seems to deter, rather than to attract, the biologist from attempting to explain organic forms by mathematical or physical law. Just as the embryologist used to explain everything by heredity, so the morphologist is still inclined to say—'the thing is alive, its form is an attribute of itself, and the physical forces do not apply.' If he does not go so far as this, he is still apt to take it for granted that the physical forces can only to a small and even insignificant extent blend with the intrinsic organic forces in producing the resultant form. Herein lies our question in a nutshell. Has the morphologist yet sufficiently studied the forms, external and internal, of organisms, in the light of the properties of matter, of the energies that are associated with it, and of the forces by which the actions of these energies may be interpreted and described? Has the biologist, in short, fully recognised that there is a borderland not only between physiology and physics, but between morphology and physics, and that the physicist may, and must, be his guide and teacher in many matters regarding organic form?

Now this is by no means a new subject, for such men as Berthold and Errera, Rhumbler and Dreyer, Bütschli and Verworn, Driesch and Roux, have already dealt or deal with it. But on the whole, it seems to me that the subject has attracted too little attention, and that it is well worth our while to think of it to-day.

The first point then, that I wish to make in this connection is, that the Form of any portion of matter, whether it be living or dead, its form and the changes of form that are apparent in its movements and in its growth, may in all cases alike be described as due to the action of Force. In short, the form of an object is a 'diagram of Forces,'—in this sense, at least, that from it we can judge of or deduce the

forces that are acting or have acted upon it; in this strict and particular sense, it is a diagram: in the case of a solid of the forces that *have* been impressed upon it when its conformation was produced, together with those that enable it to retain its conformation; in the case of a liquid (or of a gas) of the forces that are for the moment acting on it to restrain or balance its own inherent mobility. In an organism, great or small, it is not merely the nature of the *motions* of the living substance that we must interpret in terms of Force (according to Kinetics), but also the *conformation* of the organism itself, whose permanence or equilibrium is explained by the interaction or balance of forces, as described in Statics.

If we look at the living cell of an Amœba or a Spirogyra, we see a something which exhibits certain active movements, and a certain fluctuating, or more or less lasting, form; and its form at a given moment, just like its motions, is to be investigated by the help of physical methods, and explained by the invocation of the mathematical conception of force.

Now the state, including the shape or form, of a portion of matter, is the resultant of a number of forces, which represent or symbolise the manifestations of various kinds of Energy; and it is obvious, accordingly, that a great part of physical science must be understood or taken for granted, as the necessary preliminary to the discussion on which we are engaged.

I am not going to attempt to deal with, or even to enumerate, all the physical forces or the properties of matter with which the pursuit of this subject would oblige us to deal,—with gravity, pressure, cohesion, friction, viscosity, elasticity, diffusion, and all the rest of the physical factors that have a bearing on our problem. I propose only to take one or two illustrations from the subject of Surface-tension, which subject has already so largely engaged the attention of the physiologists. Nor will I even attempt to sketch the general nature of the phenomenon, but will only state

a few of its physical manifestations or laws. Of these the most essential facts for us are as follows:—Surface-tension is manifested only in fluid or semi-fluid bodies, and only at the surface of these: though we may have to interpret surface in a liberal sense in cases where the interior of the mass is other than homogeneous. Secondly, a fluid may, according to the nature of the substance with which it is in contact, or (more strictly speaking) according to the distribution of energy in the system to which it belongs, tend either to spread itself out in a film, or, conversely, to contract into a drop,—striving in the latter case to reduce its surface to a minimal area. Thirdly, when three substances are in contact (and subject to surface-tension) as when water surrounds a drop of protoplasm in contact with a solid, then at any and every point of contact, certain definite angles of equilibrium are set up and maintained between the three bodies, which angles are proportionate to the magnitudes of the surface-tensions existing between the three. Fourthly, a fluid film can only remain in equilibrium when its curvature is everywhere constant. Fifthly, the only surfaces of revolution which meet this condition are six in number, of which the plane, the sphere, the cylinder, and the so-called unduloid and catenoid are important for us. Sixthly, the cylinder cannot remain in free equilibrium if prolonged beyond a length equal to its own circumference, but, passing through the unduloid, tends to break up into spheres:—though this limitation may be counteracted or relaxed, for instance by viscosity. Finally, we have the curious fact that, in a complex system of films, such as a homogeneous froth of bubbles, three partition walls and no more always meet at a crest, at equal angles, as for instance in the very simple case of a layer of uniform hexagonal cells; and (in a solid system) the crests, which may be straight or curved, always meet, also at equal angles, four by four, in a common point. From these physical facts, or laws, the

morphologist as well as the physiologist may draw important consequences.

It was Hofmeister who first showed, more than forty years ago, that when any drop of protoplasm, either over all its surface or at some free end (as at the tip of the pseudopodium of an amœba), is seen to 'round itself off,' that is not the effect of physiological or vital contractility, but is a simple consequence of surface tension,—of the law of the minimal surface; and on the physiological side, Engelmann, Bütschli and others have gone far in their development of the idea. Plateau, I think, was the first to show that the myriad sticky drops or beads upon the weft of a spider's web, their form, their size, their distance apart, and the presence of the tiny intermediate drops between, were in every detail explicable as the result of surface-tension, through the law of minimal surface and through the corollary to it which defines the limits of stability of the cylinder; and, accordingly, that with their production, the will or effort or intelligence of the spider had nothing to do. The beaded form of a long, thin, pseudopodium, for instance of a Heliozoan, is an identical phenomenon. It was Errera who first conceived the idea that not only the naked surface of the cell, but the contiguous surfaces of two naked cells, or the delicate incipient cell-membrane or cell-wall between, might be regarded as a weightless film, whose position and form were assumed in obedience to surface-tension. And it was he who first showed that the symmetrical forms of the unicellular and simpler multicellular organisms, up to the point where the development of a skeleton complicates the case, were one and all identical with the plane, sphere, cylinder, unduloid and catenoid, or with combinations of these. Berthold and Errera almost simultaneously showed (the former in far the greater detail), that in a plant each new cell-partition follows the law of minimal surface, and tends (according to another law which I have not particularised) to set itself at right angles

to the preceding solidified wall: so giving a simple and adequate physical explanation of what Sachs had stated as an empirical morphological rule. And Berthold further showed how, when the cell-partition was curved, its precise curvature as well as its position was in accordance with physical law.

There are a vast number of other things that we can satisfactorily explain on the same principle and by the same laws. The beautiful catenary curve of the edge of the pseudopodium, as it creeps up its axial rod in a Heliozoan or a Radiolarian, the hexagonal mesh of bubbles or vacuoles on the surface of the same creatures, the form of the little groove that runs round the waist of a Peridinian, even (as I believe) the existence, form and undulatory movements of the undulatory membrane of a Trypanosome, or of that around the tail of the spermatozoon of a newt:—every one of these, I declare, is a case where the resultant form can be well explained by, and cannot possibly be understood without, the phenomena of surface-tension. Indeed in many of the simpler cases, the facts are so well explained by surface-tension that it is difficult to find place for a conflicting, much less an over-riding force.

I believe, for my own part, that even the beautiful and varied forms of the foraminifera may be ascribed to the same cause, but here the problem is a little more complex, by reason of the successive consolidations of the shell. Suppose the first cell or chamber to be formed, assuming its globular shape in obedience to our law, and then to secrete its calcareous envelope. The new growing bud of protoplasm, accumulating outside the shell, will, in strict accordance with the surface-tensions concerned, either fail to 'wet' or to adhere to the first-formed shell, and will so detach itself as a unicellular individual (*Orbulina*); or else it will flow over a less or greater part of the original shell, until its free surface meets it at the required angle of equilibrium. Then accord-

ing to this angle, the second chamber may happen to be all but detached (*Globigerina*), or, with all intermediate degrees, may very nearly wholly enwrap the first. Take any specific angle of contact, and presume the same conditions to be maintained, and therefore the same angle to be repeated as each successive chamber follows on the one before; and you will thereby build up regular forms, spiral or alternate, that correspond with marvellous accuracy to the actual forms of the foraminifera. And this case is all the more interesting, because the allied and successive forms so obtained differ only in degree, in the magnitude of a single physical or mathematical factor; in other words, we get not only individual phenomena, but lines of apparent *orthogenesis*, that seem explicable by physical laws, and attributable to the continuity between successive states in the continuous or gradual variation of a physical condition. The resemblance between allied and related forms, as Hartmann demonstrated, and Giard admitted years ago, is not always, however often, to be explained by common descent and parentage.[1]

In the segmenting egg we have the simpler phenomenon of a laminar system, uncomplicated by the presence of a solid framework; and here, in the earliest stages of segmentation, it is easy to see the correspondence of the planes of division with what the laws of surface-tension demand. For instance, it is not the case (though the elementary books often represent it so), that when the totally segmenting egg has divided into four segments, these ever remain in contact at a single point; the arrangement would be unstable, and the position untenable. But the laws of surface-tension are at once seen to be obeyed, when we recognise the little *cross-furrow* that separates the blastomeres, two and two, leaving in each case three only to meet at a point in our diagram, which point is in reality a section of a ridge or crest.

[1] Cf. Giard, 'Discours inaugurale,' *Bull. Scientif.*, iii. p. 1, 1888.

Very few have tried, and one or two (I know) have tried and not succeeded, to trace the action and the effects of surface-tension in the case of a highly complicated, multi-segmented egg. But it is not surprising if the difficulties which such a case presents appear to be formidable. Even the conformation of the interior of a soap-froth, though absolutely conditioned by surface-tension, presents great difficulties, and it was only in the last years of Lord Kelvin's life that he showed all previous workers to have been in error regarding the form of the interior cells.

But what, for us, does all this amount to ? It at least suggests the possibility of so far supporting the observed facts of organic form on mathematical principles, as to bring morphology within or very near to Kant's demand that a true natural science should be justified by its relation to mathematics.[1] But if we were to carry these principles further and to succeed in proving them applicable in detail, even to the showing that the manifold segmentation of the egg was but an exquisite froth, would it wholly revolutionise our biological ideas ? It would greatly modify some of them, and some of the most cherished ideas of the majority of embryologists ; but I think that the way is already paved for some such modification. When Loeb and others have shown us that half, or even a small portion of an egg, or a single one of its many blastospheres, can give rise to an entire embryo, and that in some cases *any* part of the ovum can originate *any* part of the organism, surely our eyes are turned to the *energies* inherent in the matter of the egg (not to speak of a presiding entelechy), and away from its original formal operations of division. Sedgwick has told us for many years

[1] 'Ich behaupte aber dass in jeder besonderen Naturlehre nur so viel *eigentliche* Wissenschaft angetroffen werden könne, als darin Mathematik anzutreffen ist.' Kant, in Preface to *Metaphys. Anfangsgründe der Naturwissenschaft* (Werke, ed. Hartenstein, vol. iv. p. 360).

that we look too much to the individuality of the individual cell, and that the organism, at least in the embryonic body, is a continuous syncytium. Hofmeister and Sachs have repeatedly told us that in the plant, the growth of the mass, the growth of the organ, is the primary fact; and De Bary has summed up the matter in his aphorism, *Die Pflanze bildet Zellen, nicht die Zelle bildet Pflanzen.* And in many other ways the extreme position of the cell-theory, that the cells are the ultimate individuals, and that the organism is but a colony of quasi-independent cells, has of late years been called in question.

There are no problems connected with morphology that appeal so closely to my mind, or to my temperament, as those that are related to mechanical considerations, to mathematical laws, or to physical and chemical processes.

I love to think of the logarithmic spiral that is engraven over the grave of that great anatomist, John Goodsir (as it was over that of the greatest of the Bernouillis), so graven because it interprets the form of every molluscan shell, of tusk and horn and claw, and many another organic form besides. I like to dwell upon those lines of mechanical stress and strain in a bone, that give it its strength where strength is required, that Hermann Meyer and J. Wolff described, and on which Roux has bestowed some of his most thoughtful work; or on the kindred conformations that Schwendener, botanist and engineer, demonstrated in the plant; or on the 'streamlines' in the bodily form of fish or bird, from which the naval architect and the aviator have learned so much. I admire that old paper of Peter Harting's, in which he paved the way for investigation of the origin of spicules, and of all the questions of crystallisation or pseudo-crystallisation in presence of colloids, on which subject Lehmann has written his recent and beautiful book. I sympathise with the efforts of Henking, Rhumbler, Hartog, Gallardo, Leduc, and others to explain on physical lines the phenomena of nuclear division.

And, as I have said, I believe that the forces of surface-tension, elasticity, and pressure are adequate to account for a great multitude of the simpler phenomena, and the permutations and combinations thereof, that are illustrated in organic form.

I might well have devoted this essay to these questions, and to these alone. But I was loath to do so, lest I should seem to overrate their importance, and to appear to you as an advocate of a purely mechanical biology. I believe all these phenomena to have been unduly neglected, and to call for more attention than they have received; but I know well that though we push such explanations to the uttermost, and learn much in the so doing, they will not touch the heart of the great problems that lie deeper than the physical plane. Over the ultimate problems and causes of vitality we shall be left wondering still.

To a man of letters and the world like Addison, it came as a sort of revelation that light and colour were not objective things but subjective, and that back of them lay only motion or vibration, some simple activity. And when he wrote his essay on these startling discoveries, he found for it, from Ovid, a motto well worth bearing in mind—*causa latet, vis est notissima.* We may with advantage recollect it, when we seek and find the Force that produces a direct Effect, but stand in utter perplexity before the manifold and transcendent meanings of that great word Cause.

The similarity between organic forms and those that physical agencies are competent to produce, still leads some men, such as Stephane Leduc, to doubt or to deny that there is any gulf between, and to hold that spontaneous generation or the artificial creation of the living is but a footstep away. Others, like Delage and many more, see in the contents of the cell only a complicated chemistry, and in variation only a change in the nature and arrangement of the chemical constituents; they either cling to a belief in

'heredity,' or (like Delage himself) replace it more or less completely by the effects of functional use and by chemical stimulation from without and from within. Yet others, like Felix Auerbach, still holding to a physical or quasi-physical theory of life, believe that in the living body the dissipation of energy is controlled by a guiding principle, as though by Clerk Maxwell's demons; that for the living the Law of Entropy is thereby reversed; and that Life itself is that which has been evolved to counteract and battle with the dissipation of Energy. Berthold, who first demonstrated the obedience to physical laws in the fundamental phenomena of the dividing cell or segmenting egg, recognises, almost in the words of John Hunter, a quality in the living protoplasm, *sui generis*, whereby its maintenance, increase, and reproduction are achieved. Driesch, who began as a 'mechanist,' now, as we have seen, harks back straight to Aristotle, to a twin or triple doctrine of the soul. And Bergson, rising into heights of metaphysics where the biologist, *quâ* biologist, cannot climb, tells us (like Duran) that life transcends teleology, that the conceptions of mechanism and finality fail to satisfy, and that only 'in the absolute do we live and move and have our being.'

We end but a little way from where we began.

With all the growth of knowledge, with all the help of all the sciences impinging on our own, it is yet manifest, I think, that the biologists of to-day are in no self-satisfied and exultant mood. The reasons that for a time contented a past generation call for re-enquiry, and out of the old solutions new questions emerge; and the ultimate problems are as inscrutable as of old. That which, above all things, we would explain baffles explanation; and that the living organism is a living organism tends to reassert itself as the biologist's fundamental conception and fact. Nor will even this concept serve us and suffice us when we approach the problems

of consciousness and intelligence and the mystery of the reasoning soul; for these things are not for the biologist at all, but constitute the Psychologist's scientific domain.

In Wonderment, says Aristotle, does philosophy begin,[1] and more than once he rings the changes on the theme. Now, as in the beginning, wonderment and admiration are the portion of the biologist, as of all those who contemplate the heavens and the earth, the sea, and all that in them is.

And if Wonderment springs, as again Aristotle tells us, from ignorance of the causes of things, it does not cease when we have traced and discovered the proximate causes, the physical causes, the efficient causes of our phenomena. For behind and remote from physical causation lies the End, the Final Cause of the philosopher, the reason Why, in the which are hidden the problems of organic harmony and autonomy, and the mysteries of apparent purpose, adaptation, fitness and design. Here, in the region of Teleology, the plain rationalism that guided us through the physical facts and causes begins to disappoint us, and Intuition, which is of close kin to Faith, begins to make herself heard.

And so it is that, as in Wonderment does all philosophy begin, so in Amazement does Plato teach us that all our philosophy comes to an end.[2] Ever and anon, in presence of the *magnalia naturae*, we feel inclined to say with the poet,

> Οὐ γάρ τι νῦν γε κἀχθὲς, ἀλλ' ἀεί ποτε
> Ζῇ ταῦτα, κοὐδεὶς οἶδεν ἐξ ὅτου 'φάνη.

'These things are not of to-day nor yesterday, but evermore, and no man knoweth whence they came.'

I will not quote the noblest words of all that come into my mind; but only the lesser language of another of the greatest of the Greeks: '*The ways of His thoughts are as paths in a wood thick with leaves, and one seeth through them but a little way.*'

D'Arcy Wentworth Thompson

[1] *Metaph.*, I. ii. 982*b*, 12, etc.

[2] Cf. Coleridge, *Biogr. Lit.*

ST ANDREWS AND SCIENTIFIC FISHERY INVESTIGATIONS

Introduction

The investigation of fish life in the sea is among the most recent developments of modern Biological Science. The University of St Andrews led the way in this work as in so many fields of intellectual activity and research.

It was appropriate that in Scotland, where sea-fishing industries rank among the first and most important in the world, her most ancient seat of learning should give the impulse to exact fisheries' research in the waters of the sea.

A lamentable lack of scientific information on fishery matters prevailed until a comparatively late date, and, as the Professor of Zoology at Cambridge (the late Professor Alfred Newton) said in closing his Michaelmas Term Lectures in 1885, 'no attempt save that of Professor M'Intosh at St Andrews has been made in this country to remove this want of knowledge.' These pioneer efforts have had fruitful and widespread results, and have greatly influenced marine investigation everywhere.

Science at St Andrews has always had a peculiar prominence. James Gregory, who invented the reflecting telescope; Napier, who gave logarithms to the world; John Goodsir, the early master of modern comparative anatomy; John Reid, the first of great Scottish physiologists; Brewster, the immortal physicist; and Lyon Playfair, the distinguished chemist, are amongst those of eminence who studied or taught at St Andrews. As was said some years ago in a leading

English serial (Macmillan's *English Illustrated Magazine*, 1889), 'In the annals of science St Andrews has no mean fame, and the names, either as students or teachers, of Edward Forbes, John Goodsir, David Brewster, John Reid, David Page, George Day, and James David Forbes, are associated with this venerable seat of Scottish culture. In the laboratories of the University, or on the beach of the far-reaching bay, these eminent men pursued their famed researches.'

Important Educational and Scientific Movements originated at St Andrews

It will surprise many persons to learn that in this retired academic centre, the British Association for the Advancement of Science had its birth, for Sir David Brewster, afterwards Principal of the United College, proposed its formation in 1831. The medical training of women began when Mrs Garrett Anderson received instruction in Anatomy from Professor Day at St Andrews in 1862, while the higher academic education of women at Girton, followed by Newnham at Cambridge, and by Somerville Hall at Oxford, received its first impetus at St Andrews. Indeed, St Andrews may be said to have originated female University education in Britain, and as long ago as 1877 the special University title of L.L.A. was granted to women by St Andrews.

Further, University Extension in Scotland was commenced by St Andrews in 1876, when Principals and Professors from the ancient Scottish University gave courses of Academic Lectures in Dundee. University College in Dundee may be said to have really originated with these first efforts on the part of the St Andrews Professoriate.

When Mr Alexander Robertson, now University Lecturer on Botany, opened a course of botanical lectures in the United College in 1892, the occasion was notable as being the first recorded admission of women to courses of regular study, on

the same conditions as men, in a Scottish University. The present writer also gave, at the same time, a course on Zoology, and in the opening address said, 'The delivery of Mr Robertson's address in the department of Botany and my own Zoological lecture to-day, mark an event in some respects unique in the academic annals of this country. . . . It remains to be seen how profoundly the great step now taken may affect the education of women in the future. . . . The part St Andrews had in the early days of Girton College, Cambridge, are well known; but all the facilities given by St Andrews and other collegiate foundations, fall short of the step, one might almost say the revolution which this quiet College witnesses now when the ancient University throws its class-rooms open to women.'

Fishery Problems first attacked at St Andrews

What was the task which St Andrews was the first to undertake in regard to fisheries, thanks to its veteran professor of Zoology Professor M'Intosh? It was, among other things, the elucidation of the many complex problems connected with fisheries and with the life of marine fishes, the discovery of the facts as to the dependence of the inshore waters upon the offshore waters, and the demonstration of the small importance of legislation, applied by the authorities to the littoral areas of the sea, from the point of view of the permanence of the fish supply in the great oceans of the world. To give an example, the cod, halibut, plaice, and turbot shed their eggs for the most part in offshore waters, and as these are pelagic and buoyant, and float freely near the sea's surface, they are largely beyond injurious interference of any ordinary kind; but, when very young, these fishes, except the haddock, seek the shores, and are too small to be seriously affected by man's operations. Nets, such as shrimpers use, destroy vast numbers of certain of these minute fishes, yet

without any evident effect on their general abundance and prevalence. In the estuary of the River Thames, shrimping nets of small mesh have been used extensively for seven hundred or eight hundred years, but the daily destruction of young soles has not led to the utter extermination of the supply of this valuable fish in the adjacent deeper waters. Fluctuations in the abundance of fishes generally are universal, but in spite of pessimistic views, complaints, and warnings, extending over two centuries, that in British waters the supply of food fishes was nearing total exhaustion, the fishing industries of the British Islands have been more extensively carried on from our principal ports than at any previous period in history.[1]

Features of Marine Research at St Andrews

Certain special features have characterised the fishery work at St Andrews, during the last thirty years, which have been of supreme value to the nation, and of the highest importance to Zoological Science. Many of the great Biological Stations, such as the famous and costly station at Naples founded in 1871, have been mainly devoted to researches of a purely technical and scientific nature, and the direct economic bearing of these researches, and their practical results in regard to the prosperity of the fisheries, have been a secondary consideration.

At St Andrews three principal features have been characteristic of the work done, namely (1) the prominence given in zoological teaching in the University to practical work; to the study of animals on the rocky shores, in the tidal pools, and in the open waters of the adjacent bay, that is to say, the study of the marine life under natural conditions, and the

[1] The exploitation of new fishing grounds, Icelandic and others, is not ignored; such exploitation being inevitable with the growth in the population of the British Isles from over 25,000,000 in 1841 to nearly 40,000,000 at the present time, seventy years later.

continuance of that study in the laboratories of the University. The marine station on the east shore at St Andrews has been of incalculable value to the University students in these laboratory studies. No other zoological school in the world could afford, so perfectly as that of this ancient University, such admirable facilities for practical study, for rock pools teeming with life and the prolific waters of St Andrews Bay, almost surround the marine station, and are within a stone's throw of the University laboratories. (2) The efforts which resulted twenty-eight years since in the securing of a temporary wooden station were, twelve years ago, crowned with complete success by the completion of the handsome Gatty Laboratory, which was opened by the Right Hon. Lord Reay on October 30, 1896. The project of a marine station at St Andrews had been kept in mind, almost since student days, by the occupant of the Chair of Natural History in the University; but it was the scientific work necessitated by the Trawling Commission which brought the matter to a practical issue. The Practical Zoological Laboratory in the University was, indeed, at first used as a marine laboratory as early as 1882. The report embodying observations made during the Trawling Commission Investigations, was referred to at length by the late Lord Playfair (then Sir Lyon Playfair), himself a distinguished St Andrews student, who said in the House of Commons that the report of Professor M'Intosh was 'one of the most valuable fishery publications ever issued.' The late Earl of Dalhousie, Chairman of the Commission, spoke of the labours involved in the preparation of this report, when moving the Sea Fisheries (Scotland) Bill, on May 21, 1885, in the House of Lords (and no man was better qualified to express an opinion), 'an eminent naturalist, Professor M'Intosh, was appointed,' said the lamented earl, 'to conduct experiments on board a steam trawler. He carried on experiments for nine months, showing much heroism and enduring a great deal of hardship in

the execution of his task.' When the handsome permanent stone buildings erected by the generosity of Dr Charles H. Gatty were opened in 1896 by Lord Reay, in the presence of a distinguished company, including leading scientific men, his lordship said, 'the first laboratory at St Andrews was entirely due to his (Professor M'Intosh's) initiation. It is to his persistent efforts that the University of St Andrews owes the existence of an institution which has made its name known and respected in the world of science. We have only to glance at the list of papers published since January 1884,' added his lordship, 'to convince ourselves of the splendid results of Professor M'Intosh's unceasing activity.'

The main object of such a laboratory was to make easy the solution of fishery problems, both marine and fresh water, and the placing of the whole subject of fisheries on a proper scientific footing, thus providing a basis for that wise and beneficial legislation which alone can preserve and improve the condition of the fishing industries. Hatching and development, and the study of the entire life and growth of most of the British food-fishes, were the first objects aimed at, and a success not surpassed, if indeed equalled, by any other institution of the kind, has resulted. That the great library of the University lies close at hand, has been of invaluable assistance to the station, and has been an advantage which probably no other laboratory in the world possesses.

(3) The proof that nature in the sea is able to cope even with the reckless destruction of the adult and young fishes by man and other destroyers. The chain of dependence, from the microscopic Diatom up through the ascending invertebrate scale to the fish, cannot be broken, it must be remembered, for the minute buoyant or pelagic nature of the eggs of the most valuable fishes in the sea, and their vast numbers, together with the protection afforded by the extent of the boundless oceanic waters, suffice for their safety. Man may remove the larger forms from a given and limited area by

his far-reaching machinery; but the oceanic waters can never be so utterly ransacked as to lead to the possibility of the total extermination of the supply of valuable food fishes. This view may, indeed, be disputed, and has been resisted by some, though not by the most eminent and experienced authorities in the world of fishery science.

Trawling Commission Work 1884

The scientific conclusions of the well-known Trawling Report of 1884 have not only received the sanction of the most eminent men of science in various countries, but have been confirmed by the later researches carried on, at great expense and with great elaboration, in the various fishing areas of Europe and of America. The conclusions were indeed carefully drawn at St Andrews, and, as just stated, have stood the test of the succeeding twenty-seven years, during which time successive able workers not only at home but abroad have entered the field. The scientific reporter, who carried on his work under the Trawling Commission's instructions in 1884, recommended the closure of certain bays for experimental purposes. This was done, and the work involved in tests and observations was placed by Lord Dalhousie in the hands of the Fishery Board for Scotland. This Board for ten years carried out, by means of the steamer *Garland*, the investigation of the areas set apart. These investigations were made at stated intervals, and on prescribed lines, as arranged by the original reporter (Professor M'Intosh). Later, the Scientific Superintendent of the Board reported and compared the first five with the last five years, but, it is to be noted, that in contrasting the periods which differed essentially in regard to seasons of work, he made a somewhat serious error, for the first five years' work was done mostly in the warmer season, and the last five mainly in the colder season of the year. Accordingly the conclusion resulting,

namely, that this amount of trawling in the closed areas showed a diminution in the fish-fauna from first to last, was a very large conclusion to draw from very slender premises. The mistake was pointed out at once by the scientific expert of the Trawling Commission in his *Resources of the Sea*, though a number of workers new to fishery investigations at Plymouth, and some other writers attempted to support the theory of the 'impoverishment' of the sea. The view has been, however, generally abandoned, and a return made to the St Andrews views, even the International Scientific Workers having refrained from giving prominence to the wholly unjustifiable conclusion that the world's supply of sea fish might be endangered by the operations of man. The plan of the International Investigations conducted for nearly ten years in the North Sea, was chiefly arranged by certain British representatives, who had expressed very strong views as to the alleged impoverishment of the sea; but, having apparently receded from that position, these marine investigations, costing up to the present time the large amount of £60,000 or £70,000, have confirmed merely what was already pronounced to be scientific fact, and proved to be so by the investigations of a quarter of a century ago.

The labours of the band of workers carrying on original researches under the stimulus of the present Professor of Zoology in the University, who has also been from the commencement the head of the St Andrews Marine Laboratory, have yielded results so important that no fishery memoir of any note, no work on the life-history of marine fishes in any country, has failed to make allusion, and usually lengthy allusion, to the remarkable pioneer work carried on for thirty years at St Andrews, and still actively pursued there. Even when unacknowledged, it is known that much of the best work in England, Ireland, Germany, Canada, South Africa, and other countries has been based on the famous St Andrews researches. It is true that, now and then, some report or

scientific memoir may embody work done on other lines, or even on lines opposed to those adopted at St Andrews, but it is only fair to the Scottish Laboratory to say that in no case has such work proved fully reliable, or of any real permanent utility to those charged with the onerous task of administering fisheries, or framing fishery legislation for the preservation of the resources of the sea and of inland waters. Much reliable work has been done by various investigators, and a mass of reports issued from different laboratories, which merely repeat, in some cases almost without alteration, the discoveries made at St Andrews; and the later descriptions and drawings of eggs and larvæ, and the more mature stages, are frequently little different from those issued during the last quarter of a century from the Marine Laboratory at St Andrews. A large amount of public money devoted to such work—work which had already been done by the St Andrews experts—might have been devoted to new and more fruitful researches. It is mere justice to say that the St Andrews researches, for a long period, were made with much sacrifice on the part of all engaged, and with very meagre support from the public funds. So many vital problems still urgently await solution in regard to the sea's resources, that the mere repetition, under public auspices, of work already done, is too serious a matter to go unnoticed. The public have not yet awakened to the unjustifiable diversion of public money, in carrying on such unnecessary work, or in pursuing elaborate investigations which have no bearing on the prosperity of the fisheries, as a great national industry and a source of food supply for the people.[1]

[1] As an example of unnecessary research and wasteful costly publication, it may be pointed out that at least five detailed accounts (the latest in German) of the eggs and development of the Plaice (*Platessa*) have appeared in recent years, accompanied by costly plates and drawings, these differing little from the drawings and plates published from St Andrews over twenty years ago.

St Andrews Furnished First Basis for Later Work

Elaborate notes on the food of fishes collected during a long period, chiefly by the head of the Marine Laboratory, and supplemented by the additions made by successive workers at St Andrews, have formed the basis of all subsequent work in this important line of study. Reference to a well-known paper, read at the Fisheries Exhibition Conference, London, 1883, by the late Dr Francis Day, upon the subject of the food of fishes, shows clearly how much Professor M'Intosh's published researches were depended upon, indeed it may be said that the pioneer work in this important branch of study was commenced long ago at St. Andrews. Further, the systematic study of 'Plankton' or the minute floating life in St Andrews Bay, month by month, for a lengthy period, constituted the groundwork of later labours in that important field of investigation. From St Andrews numerous papers on the surface fauna of the sea, and also of the deeper regions, in successive seasons, testify to an incredible amount of toil and close observation. The importance of this work can only be realised when it is remembered that the illimitable swarms of living organisms, scattered through the various strata of the sea, constitute the food of all our important fishes during their early life, and largely form the food of the invertebrates upon which the fishes mainly feed in their full-grown condition.

One great advantage that sea fishery investigators have had at St Andrews, arises from the fact that St Andrews Bay is a compact and definite area in which the extent of fishing operations can be approximately determined and checked, in contrast to the outside waters where difficulty arises owing to the extent of fishing operations and to the conditions in the open sea. Indeed, a unique grasp of the situation was afforded by a long period of sixty years' actual experience of

the Bay of St Andrews on the part of the head of the station, and has sufficed to show how different was the true interpretation of some of the results of experiments, especially trawling experiments, carried on under Government auspices, from the interpretations and conclusions published with official sanction from time to time in recent years. Reference has already been made to the remarkable conclusion published in the Scottish Fishery Board's Reports, by able and high officials, where years were compared in which the Government boat carried on experiments in the warm season with those in which experiments were carried on in the cold season, a course which rendered unreliable conclusions inevitable. All unbiassed observations, since the publication of these results in 1896, have confirmed the view taken at St Andrews based on accurate scientific observations, and backed up by long practical experience of the fisheries of the Scottish coast.

In every country possessed of fisheries, the officials, charged with responsible administration, have felt the need of accurate conclusions based upon exact and unbiassed research. The St Andrews researches have afforded such a basis, partially at any rate, and it is generally recognised abroad that Lord Reay expressed the truth when he said at St Andrews, 'It is quite clear that no good can result from legislation which does not take into account the results of scientific enquiries which are prosecuted in this laboratory. A glance at the papers published since 1884 shows,' His Lordship added, 'how important their contents are for those who wish to protect our fisheries. It is an indirect result, but it increases our gratitude to those who have been absolutely disinterested in securing it.' None know better the value of the St Andrews fishery investigations during the last thirty years, it may be repeated, than those who have the superintendence of great fishery resources and vast fishing industries, such as those of Canada, or of the United States,

and, in a less degree, of South Africa, Australia, or India. It is true that in much fishery legislation, even in Britain, the important investigations at St Andrews have been ignored on other than scientific grounds, and apparently their very existence not recognised or known to the authorities; but in other parts of the British Empire their value is fully appreciated, and in the United States reference is often made to them, while in France, Germany, and Italy all the authorities attach great value to them.

The Marine Station, fortunately, has been able to carry on its surprisingly important work at St Andrews with very slight aid, and indeed without any since 1896, from the more than ample resources provided by the British Government for fishery investigations. This condition of things appears almost incredible, for it was Lord Reay who pronounced it to be an institution in the service of science of the highest importance. 'It ranks,' he affirmed, 'amongst the most valuable of the marine laboratories of the world.' As was said twenty years ago, in an article already alluded to, 'with extension and further development, the well-nigh unique conditions it can boast bid fair to make it one of the most valuable and interesting scientific institutions of the kind in existence.' Lord Reay recognised its value when he said, 'The Laboratory ranks amongst the most prominent scientific institutions of Scotland. It is one of the principal connecting links of our Universities with those of other countries.' [1]

Published Results of St Andrews Investigations

From St Andrews there have issued, in a long and interesting succession, papers of the most important scientific character numbering close upon five hundred. Up to 1896 no less than three hundred and thirty-nine of these papers had been issued from the St Andrews Station, almost all on

[1] *English Illustrated Magazine*, July 1889.

Marine Zoological subjects. Since then, as just intimated, the number has been greatly increased, but, of these three hundred and thirty-nine papers, seventy-one were published before the founding of the Marine Biological Station, and extend over a period from 1848 to 1882. After January 1884 two hundred and sixty-eight papers appeared up to 1896, and of these one hundred and eighty-one relate particularly to fish and fisheries, while eighty-seven deal with other zoological subjects. A complete list of the titles of these memoirs and papers, however interesting they might be to the scientific specialist, would not be altogether appropriate in the present brief review, and it must suffice to merely refer to the names of the more prominent workers who have occupied tables in the Marine Station and have carried on researches at St Andrews.

Many of these have been trained in the Biological Department of the University, while a considerable proportion have come from other Universities, and from distant countries, to engage in original investigations.

Abbreviated List of Biological Investigators at St Andrews since 1880

The list includes Sir J. Burdon Sanderson; Professor Francis Gotch of Oxford; Dr R. F. Scharff, head of the National Museum, Dublin; Professor John Cleland, Glasgow; Professor Ernst Haeckel, Jena; Professor A. W. W. Hubrecht, Utrecht; Dr John Wilson, St Andrews; Dr R. Kennedy, Glasgow; Dr Marcus Gunn, London; Professor W. F. R. Weldon, Cambridge; Professor A. G. Bourne, Oxford; Dr H. E. Durham, London; Mr W. L. Calderwood, Edinburgh; Mr E. W. L. Holt, Scientific Adviser to the Board of Agriculture and Fisheries, Dublin; Mr J. Pentland Smith, Swanage; Professor J. Lindsay Stephen, Glasgow; Rev. A. D. Sloan, St Andrews; Mr W. E. Collinge, Birmingham; Professor J. D. F. Gilchrist, Cape Town, South Africa; Dr A. T.

Masterman, H.M. Inspector of Fisheries, London; Dr H. Charles Williamson, Scientific Department, Fishery Board for Scotland; Mr G. Sandeman, Edinburgh; Dr J. H. Fullarton, Glasgow; Dr Henry Bury, Cambridge; Professor A. P. Knight, Queen's University, Kingston, Canada; Professor D. J. Cunningham, University of Dublin; Professor Purser, University of Dublin; Dr J. R. Tosh, lately Government Zoologist, Queensland; Dr Alford Anderson, St Andrews; Dr William Wallace, Scientific Department, Board of Agriculture and Fisheries, London; Dr H. M. Kyle, Bureau de Conseil Internationale pour l'Exploration de la Mer, Copenhagen; Dr W. G. Ridewood, British Museum; Dr Fraser Harris, University of Birmingham; Dr J. Cameron, Lecturer on Anatomy, London; Dr Robert Marshall, Java; Dr H. W. Marett Tims, Cambridge and London; Dr J. Rennie, Aberdeen; Dr William Nicoll, Lister Institute, London; Dr Swinnerton, University College, Nottingham; Mr J. B. Buist, Dundee; Professor R. C. Punnett, Cambridge; Dr Cyril Crossland; Mr J. H. Crawford, and the present writer.

The list is by no means inclusive, for, almost without exception, the students in the University who pursue zoological and botanical studies, spend part of their time in practical work in the laboratories and in the Marine Station, and many of them have, by these studies, attained distinction.

Conclusion

Almost exactly thirty years ago,[1] Professor M'Intosh pointed out that 'in connection with zoological researches on the structure and development of marine animals, there is no greater defect in our country than the absence of Zoological Stations, at which such investigations can be carried on.' Oxford and Cambridge had no such station,

[1] Introductory Lecture, University of St Andrews, November 13, 1882.

no Scottish University had established one; yet, added the eminent authority referred to, 'there are few sites in this or any other country . . . better adapted, on the whole, for a combined zoological station and laboratory than St Andrews. The proximity of the city to the sea, its quietude—so conducive to study—and the valuable library and museum of the University, on the one hand; and on the other the fine stretch of sand on which so many rare specimens are thrown by storms, sufficiently demonstrate the position.' The important fisheries' work accomplished, and the splendid record of biological work done, have amply justified the claim to the supremacy of St Andrews in marine research.

EDWARD ERNEST PRINCE

ON THE TOXICITY OF LOCAL ANÆSTHETICS

One of the most interesting chapters in pharmacology is the discovery and development of the group of drugs acting as local anæsthetics. Thirty years ago the only method of producing local anæsthesia was by means of the ether spray; to-day we know of many drugs which act more or less specifically on sensory nerves, and some of which are used to produce anæsthesia not only for the minor but also for the major operations of surgery.

Of this group of specific local anæsthetics cocaine was the first and for some time the only member. Isolated in 1860 by Niemann,[1] it was stated by him to produce, on tasting, numbing of the sensibility of the tongue. This effect was corroborated by de Marle,[2] Lossen,[3] and Moreno-y-Mays.[4] It was not, however, until 1880 that the local anæsthetic action of cocaine was definitely demonstrated. Then von Anrep[5] found that, after injecting a 0·6 per cent. solution of the hydrochloride under the skin of his arm, the part became insensitive to the pricking of a needle, and remained so for nearly half an hour. He further observed that the painting of the tongue with a 1 per cent. solution caused loss of sensibility and loss of the sense of taste over the painted area; and that after injection into a frog the sensory nerves lost their irritability before the motor nerves. He suggested the

[1] Liebig's *Annalen*, cxiv. p. 213 (1860).

[2] (1862), quoted in Schmiedeberg's *Pharmakologie*.

[3] Liebig's *Annalen*, cxxxiii. p. 358 (1865).

[4] *Thèse de Paris*, 1868, quoted by von Anrep; Schmiedeberg, *Pharmakologie*; etc.

[5] Pflüger's *Archiv*, xxi. p. 38 (1880).

use of cocaine as a local anæsthetic; but the suggestion was not immediately adopted. It was not until Koller [1] showed, four years later, that instillation of a cocaine solution into the eye induced sufficient anæsthesia of the cornea to enable operations on the eye to be painlessly performed, that the drug came into general use as a local anæsthetic. Unfortunately in not a few cases its use led to serious consequences.[2] Alarming symptoms and some deaths were ascribed to it; and this, coupled with the facts that in some cases it also produced undesirable local effects, that it was expensive, and that its aqueous solutions did not keep well and decomposed on prolonged boiling,[3] thus precluding what was regarded as efficient sterilisation, led to the desire for a more stable and less toxic substitute. With one exception (tropacocaine) no substitute of enduring value, however, was found until the chemical constitution of cocaine had, to a large extent, been determined.

In 1862, two years after the isolation of cocaine, Lossen [4] showed that it was methyl-benzoyl-ecgonine; and no further advance in its chemistry seems to have been made until after Koller's demonstration of its value as a local anæsthetic. Then the work was actively pursued, especially by Einhorn [5] and his pupils. In the course of his investigations Einhorn showed that anhydroecgonine could be decomposed into tropidine and carbon dioxide [6]; and he thus established the close connection between atropine and cocaine—a connection,

[1] *Wien. med. Woch.*, 1884, pp. 1276, 1309.

[2] Falk (*Therap. Monatsh.*, iv. p. 511 (1890)) collected 176 cases of acute cocaine intoxication, of which ten were fatal, during the first six years of its use.

[3] Paul (*Pharmac. Journ.*, 3 ser., xvi. p. 325 (1885)). He was apparently of opinion that benzoyl-ecgonine was possibly formed. This was proved to be the case by Einhorn (*Ber. d. deut. chem. Ges.*, xxi. p. 47 (1888)).

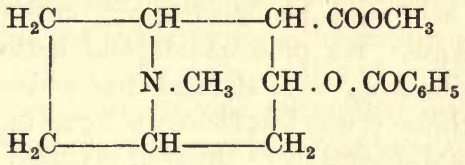
[4] Liebig's *Annalen*, cxxxiii. p. 351 (1865).

[5] *Ber. d. deut. chem. Ges.*, xx. p. 1221 (1887); xxi. pp. 47, 3029, 3441 (1888); xxii. pp. 399, 1362, 1495 (1889); xxiii. pp. 468, 979, 1338, 2889 (1890); xxvi. pp. 324, 1482 (1893); xxvii. pp. 1523, 1874, 1880, 2439 (1894).

[6] *Ber. d. deut. chem. Ges.*, xxi. p. 3029 (1888).

curiously enough, casually referred to by Niemann[1]—which has played so large a part in the determination of the constitution of cocaine, and even in the preparation of the first synthetic substitutes for cocaine.

The earliest constitutional formula for cocaine was based upon the formula for tropine suggested by Ladenburg.[2] Some years later this tropine formula was shown by Merling [3] to be insufficient to explain its reactions, and it was not until 1897-98 that the formulæ of tropine and ecgonine was established by Willstätter.[4] According to him these bases contain a N.methyl-pyrrolidine and a N.methyl-piperidine ring united to form a cyclo-heptane nucleus, which he termed tropan. Ecgonine is the β.carboxylic acid of tropine, and when methylated and benzoylated yields cocaine.



Cocaine

Pari passu with the investigations on the chemical constitution of cocaine, a large number of derivatives of cocaine were tested physiologically. Most of these were found to be inactive or only slightly active as local anæsthetics ; a few appeared to be more powerful than cocaine, but as they were also more irritant they could not be used as substitutes for this substance. Two noteworthy views, however, resulted from some of these investigations. Filehne [5] came to the conclusion that the benzoyl radical was the most important factor in a local anæsthetic ; whereas it would appear from the

[1] Liebig's *Annalen*, cxiv. p. 216 (1860).

[2] *Ber. d. deut. chem. Ges.*, xv. p. 1031 (1882) ; xx. p. 1647 (1887).

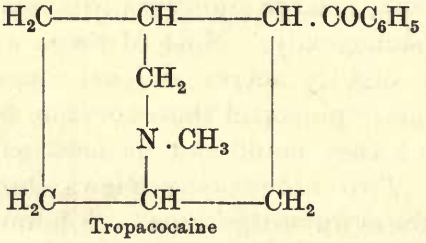
[3] *Ber. d. deut. chem. Ges.*, xxiv. p. 3108 (1891).

[4] *Ber. d. deut. chem. Ges.*, xxx. p. 2679 (1897) ; xxxi. pp. 1202, 1534, 2498, 2655 (1898).

[5] *Berlin. klin. Woch.*, 1887, p. 107.

researches of Stockman [1] and Poulsson [2] that esterification is the essential feature. Neither view is universally true, but both have had an important bearing on the search for substitutes for cocaine. A third point of importance which appears to have been established is that the presence of a phenolic hydroxyl confers irritant properties on a substance, and is consequently best avoided. Recently [3] evidence has been brought forward to show that the principle of partition-coefficients plays an important part in the action of local anæsthetics, but so far this view has had no influence on the production of substitutes for cocaine.

The first substitute of real value was not synthetically prepared, but was isolated from Java coca leaves by Giesel.[4] It was shown by Liebermann [5] to break up, on hydrolisation, into benzoic acid and pseudo-tropine, and was termed by him tropacocaine. Its pharmacological action was investigated by Chadbourne,[6] who showed that while being a powerful local anæsthetic it was less toxic than cocaine, and possessed certain actions differing from those of cocaine. As a result of his researches, Liebermann gave to it the following constitutional formula :—

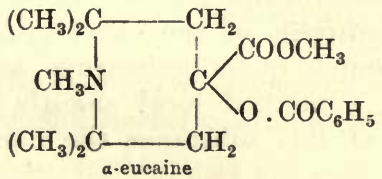


Tropacocaine

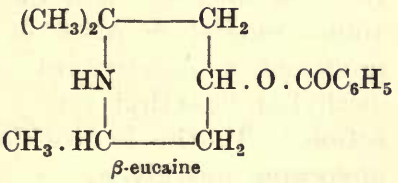
The first synthetic substitute for cocaine was obtained as the result of investigations on the pharmacological influence

[1] *Pharmac. Journ.* (3), xvi. p. 897 (1886); *Journ. Anat. Physiol.*, xxi. p. 46 (1886).
[2] *Arch. f. exp. Path. u. Pharmak.*, xxvii. p. 301 (1890).
[3] Gros, *Arch. f. exp. Path. u. Pharmak.*, lxii. p. 380; lxiii. p. 80 (1910).
[4] *Pharmazeut. Zeitung.*, July 4, 1891; quoted by Liebermann and by Chadbourne.
[5] *Ber. d. deut. chem. Ges.*, xxiv. p. 2336 (1891); with Limpach, xxv. p. 927 (1892).
[6] *Brit. Med. Journ.*, 1892, ii. p. 402.

of various groupings in atropine and cocaine. In 1883 Emil Fischer,[1] working with the triacetonalkamine obtained by Heintz, came to the conclusion that it was a tetra-methyl-oxypiperidine, and he noticed further that on heating the substance it lost a molecule of water, and became changed into a base, which he termed triacetonine. As this behaviour was very similar to that shown previously by Ladenburg in the case of tropine, it suggested a close relationship between triacetonamine and tropine. And, on the analogy of homatropine (mandelyl-tropeine) Fischer combined triacetonamine with mandelic acid, and found that, like homatropine, the new substance produced dilatation of the pupil when applied to the eye. Thirteen years later, when the similarity in the constitution of atropine and cocaine was known, Merling prepared a number of alkyl-benzoyl compounds of the carboxylic acid of triacetonamine, and gave them to Vinci [2] for pharmacological investigation. As was expected, some of these produced local anæsthesia, and one (N.methyl-benzoyl-tetramethyl-γ.oxy-piperidine carboxylic acid methyl ester), which was found to be considerably less toxic than cocaine, was introduced as a local anæsthetic under the name eucaine. Later, a similar compound was prepared from vinyl-diacetonamine, and was found to be less toxic and less irritant than eucaine.[3] It was introduced into therapeutics as eucaine B. It is benzoyl-trans-vinyl-diacetonalkamine, and is now known as beta-eucaine.



α-eucaine



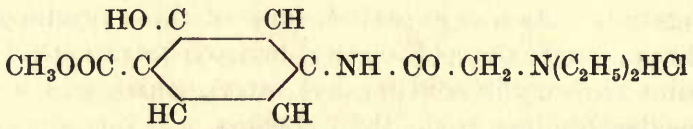
β-eucaine

These investigations led to similar preparations being made

[1] *Ber. d. deut. chem. Ges.*, xvi. p. 1604 (1883).
[2] Virchow's *Archiv*, cxlv. p. 78 (1896).
[3] Vinci, Virchow's *Archiv*, cxlix. p. 217 (1897).

with the pyrrolidine ring[1] instead of the piperidine ring as a nucleus, and these also were found to produce local anæsthesia, but as they did not possess any advantages over substances already known, they were not introduced into practice.

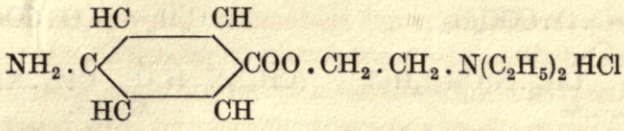
Further work on the subject followed somewhat different lines. Einhorn and Heintz showed that the alkyl-esters of amido-oxybenzoic acids possess local anæsthetic properties, and they introduced p.amino-m.oxybenzoic acid methyl ester under the name orthoform,[2] and, later, m.amino-p.oxybenzoic acid ethyl ester under the name orthoform-neu.[3] Both are too insoluble in aqueous solutions and their salts are too irritant to be considered as substitutes for cocaine; but by introducing glycocoll more soluble and less irritant compounds were obtained, and the hydrochloride of diethyl-amino-acetyl-p.amino-o.oxybenzoic acid methyl ester was recommended, under the name nirvanine, as a local anæsthetic.[4]



Nirvanine.

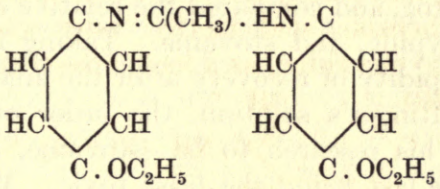
Later Ritsert discovered that p.amino-benzoic acid ethyl ester was anæsthetic to nerve-endings, and he introduced this substance as anæsthesin and its p.phenol-sulphonic acid salt as subcutin. The former is too insoluble and the latter too irritant to permit of their being regarded as valuable substitutes for cocaine. But the further introduction of a diethyl-amino radical in place of a hydrogen of the ethyl group produced a non-irritant compound (p.amino-benzoic acid diethyl-amino-ethyl ester) with a marked local anæsthetic action.[5] To the hydrochloride of this substance the name novocaine was given.

[1] Pauly, Liebig's *Annalen*, cccxxii. p. 92 (1902).
[2] *Münch. med. Woch.*, xliv. p. 931 (1897).
[3] *Münch. med. Woch.*, xlv. No. 42 (1898).
[4] *Münch. med. Woch.*, xlv. p. 1553 (1898).
[5] Cf. Braun, *Deut. med. Woch.*, 1905, ii. p. 1669.



Novocaine.

Another group of local anæsthetics may be regarded as phenetidine derivatives. The slight analgesic action of phenetidine compounds was found to be considerably increased by combining two molecules; and the hydrochloride of one compound thus formed has been used in surgical practice. It is known as holocaine, and is obtained by condensing p.phenetidine and phenacetin and converting the product into the hydrochloride.[1] Chemically it is diethoxy-diphenyl-ethenylamide hydrochloride.



Holocaine (base)

The last group of substances requiring notice was introduced by Fourneau.[2] In the course of a chemical investigation of some new amino-alcohols he found that they possessed a well-marked local anæsthetic action. One of them, now known as stovaine—the hydrochloride of dimethyl-amino-dimethyl-ethyl-carbinol benzoic acid ester—was investigated clinically and pharmacologically by Lapersonne,[3] Chaput,[4] Launois and Billon,[5] and Pouchet,[6] and as a result of their researches has been largely used in practice. By the introduction of a second dimethyl-amino group in place of a hydrogen

[1] *Centralblatt. f. pract. Augenheilk.*, 1897, pp. 30, 53, 55.

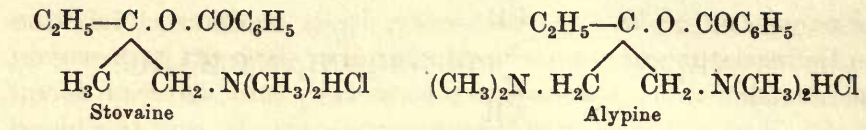
[2] *Comptes Rendus de l'Acad. des Sci.*, cxxxviii., p. 767 (1904).

[3] *Presse Médicale*, 1904, p. 233.

[4] *Compt. Rend. Soc. de Biol.*, lvi. p. 770 (1904).

[5] *Compt. Rend. de l'Acad. des Sci.*, cxxxviii. p. 1360 (1904).

[6] *Bull. Acad. de Med.* (3), lii. p. 110 (1904).



of the methyl group of this compound another local anæsthetic, named alypine, was obtained.[1]

The toxicity of these various substances was determined previous to their introduction into therapeutics, and in most cases it was compared with and found to be less than that of cocaine. During the last few years, mainly owing to the employment of these compounds to produce spinal anæsthesia, the question of their relative toxicity has assumed greater importance, and several and varied investigations have been made with this end in view. Laewen [2] employed the sciatic nerve of the frog, and compared the relative effects of cocaine, novocaine, alypine, and stovaine. Taking into account the degree and rapidity of recovery after the anæsthetic had been replaced by Ringer's solution, the order of toxicity would appear from his research to be—stovaine, alypine, cocaine, novocaine, the last being the least toxic. More recently, Le Brocq [3] has determined the toxicity of various local anæsthetics on frogs, mice, and rabbits. Assuming the toxicity of cocaine to be represented by 1·0, he concludes that the toxicity of the other substances may be represented as follows: —alypine, 1·25; nirvanine, 0·714; stovaine, 0·625; tropacocaine, 0·500; novocaine, 0·490; beta-eucaine lactate, 0·414.

My own experiments were made previous to the publication of the last-mentioned paper, and the observations were limited to the relative effects on the circulation and respiration, as it is mainly through these systems that these drugs produce their most serious ill-effects. As only a relative effect was required, the whole of the experiments were made on etherised rabbits. The blood-pressure was taken from the common carotid artery, and the respiration was recorded by means of a

[1] Impens, *Deut. med. Woch.*, 1905, ii. p. 1154.

[2] *Arch. f. exp. Path. u. Pharmak.*, lvi. p. 138 (1907).

[3] *Brit. Med. Journ.*, 1909, i. p. 783.

phrenograph or, in two cases only, by a tambour connection to the exit tube of the tracheal cannula. The drug, dissolved in normal saline, was injected into the right anterior facial vein. As the degree of concentration of the drug in the blood in the heart and the medulla is a very important factor in this kind of experiment, care was taken to make the injections in each experiment as uniform in duration as possible, and, to obtain this, different dilutions of the different drugs were employed.

The substances investigated were cocaine, tropacocaine, β.eucaine, holocaine, stovaine, alypine, nirvanine, and novocaine. They all produce, when administered in sufficient quantity, diminution in the extent and slowing of the respiration, and almost invariably a fall of blood-pressure. In relatively small doses cocaine, and to a less extent and less constantly stovaine, cause a rise in blood-pressure, but in such doses the respiration is not as a rule materially affected. On the other hand, large doses (0·003 g.) of the more potent drugs, such as cocaine and alypine, cause almost immediate cessation of the respiration and a marked and rapid fall of blood-pressure, and the animal quickly dies. For the purpose of comparing the relative action of these compounds, it is desirable to employ doses producing distinctive effects from which complete or considerable recovery occurs. This allows of repeated doses of different drugs being given to the same animal; and this is especially necessary because, as previous observers have shown and the same was noted in my own experiments, different animals often react somewhat differently, at least quantitatively, to this class of drugs.

An analysis of the tracings obtained seems to show that, as regards their effect on the circulation and respiration, the order of toxicity, commencing with the most potent, is (*a*) cocaine; (*b*) alypine; (*c*) holocaine, stovaine, tropacocaine; (*d*) β-eucaine; (*e*) nirvanine and novocaine. And if, following Le Brocq, numerical values may be ventured upon, the relative toxicity of the various substances may be said to be approxi-

mately as follows:—cocaine, 1·0; alypine, 0·9; holocaine, 0·6; stovaine, 0·55; tropacocaine, 0·5; β-eucaine, 0·4; nirvanine and novocaine, 0·3. These numbers differ somewhat from those given by Le Brocq, but considering the different methods employed there is considerable agreement in the results. To a large extent the differences, with the possible exception of nirvanine, can be explained by differences in the rapidity of absorption after hypodermic administration, which was the method he employed.

Two illustrative protocols of experiments are given. It is only necessary to remark that the effect of alypine and cocaine shown in the first experiment is less than that obtained in any other experiment with the concentrations mentioned.

RABBIT: 1850 grammes: Ether: Blood-pressure from Right Common Carotid Artery: Injection into Right Anterior Facial Vein: Respiration taken by means of a Phrenograph.

Time	Blood-pressure in Mm. Hg.	Number of Respirations in five Secs.	Height of Respiratory Curve in Mm.	Remarks
3–40′–30″	112	7·8	10	
3–40′–35″	..	..	..	1 cc. 1/300 tropacocaine hydrochloride injected.
3–40′–45″				
3–40′–50″	94	6·8	9	
3–41′–10″	112	6·2	10	
3–41′–30″	113	7·4	9·2	
3–48′–20″	113	5·5	8·5	
3–48′–30″	..	..	..	1 cc. 1/300 stovaine injected.
3–48′–42″				
3–48′–50″	98	3·8	11·0	
3–49′–10″	112	4·2	12	
3–50′	108	5·0	11·2	More ether.
3–59′–30″	100	8·0	7·5	
3–59′–40″	..	..	..	1 cc. 1/300 holocaine injected.
3–59′–52″				
4– 0′	76	4·0	5·0	
4– 0′–10″	82	6·0	3·5	
4– 0′–20″	88	7·5	2·5	
4– 2′	..	..	..	Artificial respiration for 1 minute.

Experiment continued.

Time	Blood-pressure in Mm. Hg.	Number of Respirations in five Secs.	Height of Respiratory Curve in Mm.	Remarks
4– 9′–10″	103	7·2	9·0	
4– 9′–20″	..	..	..	1 cc. 1/300 β-eucaine injected.
4– 9′–29″				
4– 9′–40″	83	6·5	8·0	
4–10′	98	6·0	11·0	
4–16′–10″	88	6·6	8·5	
4–16′–20″	..	..	..	1 cc. 1/500 alypine injected.
4–16′–30″				
4–16′–40″	70	5·8	8·0	
4–17′	77	5·0	9·5	
4–18′	87	5·7	9·0	
4–23′–10″	87	6·0	7·0	
4–23′–20″	..	..	..	1 cc. 1/700 cocaine hydrochloride injected.
4–23′–29″				
4–23′–40″	91	5·8	6·8	
4–24′	96	6·0	7·0	
4–25′	89	6·6	7·5	
4–29′–20″	75	6·6	8·0	
4–29′–25″	..	..	..	1 cc. 1/500 cocaine hydrochloride injected.
4–29′–34″				
4–30′	82	6·6	7·5	
4–31′	83	7·0	8·0	
4–34′	75	7·3	8·8	
4–36′–10″	82	7·2	8·0	
4–36′–20″	..	..	..	1 cc. 1/500 alypine injected.
4–36′–28″				
4–36′–40″	65	6·2	6·7	
4–37′–30″	80	6·5	7·5	
4–39′	84	7·2	8·0	
4–41′–10″	84	7·2	8·0	
4–41′–15″	..	..	..	1 cc. 1/300 tropacocaine hydrochloride injected.
4–41′–23″				
4–41′–35″	65	6·2	7·0	
4–43′	90	7·5	7·2	

RABBIT: 1500 grammes: Ether: Procedure as in previous Experiment.

Time	Blood-pressure in Mm.Hg.	Number of Respirations in five Secs.	Height of Respiratory Curve in Mm.	Remarks
11–57′	112	14	3·5	
11–57′–10″	..	..	..	1 cc. 1/400 alypine injected.
11–57′–25″				
11–57′–30″	63	12·6	4·0	
11–57′–40″	45–55	11·0	2·0	
11–58′–50″	45–57	11·5	1·0	
11–59′–30″	76	13·5	2·7	
12– 0′	87	14·0	3·7	
12– 3′	109	12·0	4·8	
12–10′–10″	117	9·2	5·3	
12–10′–20″	..	..	..	1 cc. 1/600 cocaine hydrochloride injected.
12–10′–40″				
12–10′–50″	77–86	9·8	4·0	
12–11′–30″	70–84	11·5	2·5	
12–12′	106	11·7	4·0	More ether.
12–20′	..	..	..	The above injections repeated with similar result.
12–35′				
12–41′–40″	82	8·0	7·0	
12–41′–50″	..	..	..	1 cc. 1/300 β-eucaine injected.
12–42′–10″				
12–42′–20″	73	7·5	6·8	
12–43′	80	7·5	6·5	
12–47′–40″	90	7·8	5·0	
12–47′–50″	..	..	..	1 cc. 1/100 novocaine injected.
12–48′–12″				
12–48′–25″	59	5·4	3·5	
12–49′	86	6·2	3·8	
12–52′–10″	96	9·4	4·0	
12–52′–20″	..	..	..	1 cc. 1/100 holocaine injected.
12–52′–46″				
12–52′–55″	45	2·2	7·5	
12–53′–10″	34	3·0	6·0	
12–54′	34	4·0	1·0	No recovery.

CHARLES ROBERTSHAW MARSHALL

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